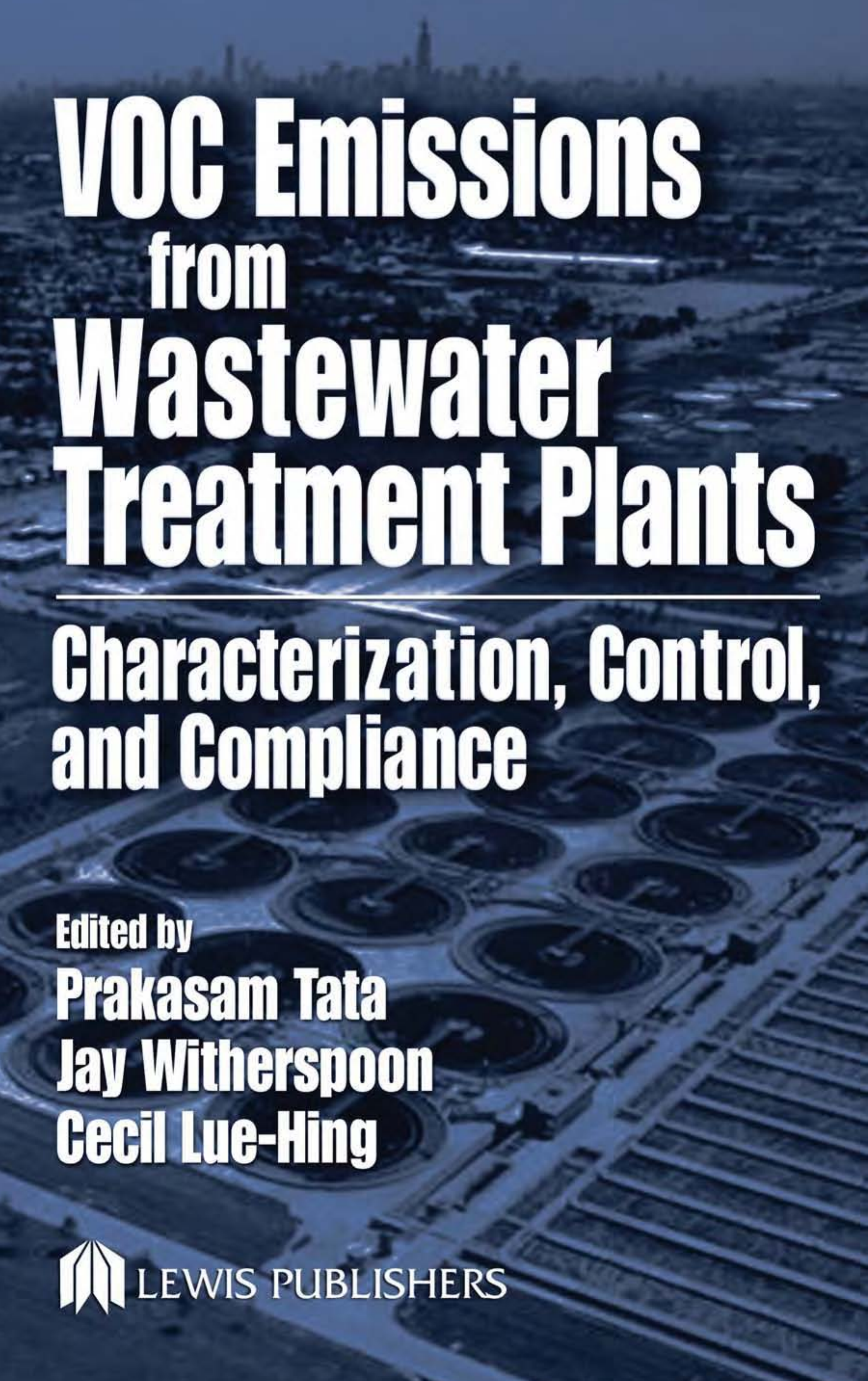


VOC Emissions from Wastewater Treatment Plants

Characterization, Control, and Compliance

Edited by

Prakasam Tata
Jay Witherspoon
Cecil Lue-Hing

LEWIS PUBLISHERS

VOC Emissions from Wastewater Treatment Plants

Characterization, Control, and Compliance

VOC Emissions from Wastewater Treatment Plants

Characterization, Control, and Compliance

Edited by

Prakasam Tata
Jay Witherspoon
Cecil Lue-Hing

LEWIS PUBLISHERS

A CRC Press Company
Boca Raton London New York Washington, D.C.

Library of Congress Cataloging-in-Publication Data

Tata, Prakasam
VOC emissions from wastewater treatment plants : characterization, control, and compliance / Prakasam Tata, Jay Witherspoon, Cecil Lue-Hing
p. cm.
Includes bibliographical references and index.
ISBN 1-56676-820-9 (alk. paper)
1. Sewage disposal plants--Environmental aspects--United States. 2.Volatile organic compound--Environmental aspects--United States. 3. Air quality management--United States. I. Witherspoon, Jay. II. Lue-Hing, Cecil. III. Title.
TD888.S38T38 2003
628′.3 028‘6—dc21 2002041502
CIP

This book contains information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Reasonable efforts have been made to publish reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage or retrieval system, without prior permission in writing from the publisher.

All rights reserved. Authorization to photocopy items for internal or personal use, or the personal or internal use of specific clients, may be granted by CRC Press LLC, provided that $.50 per page photocopied is paid directly to Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923 USA. The fee code for users of the Transactional Reporting Service is ISBN 1-56676-820-9/01/$0.00+$1.50. The fee is subject to change without notice. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

The consent of CRC Press LLC does not extend to copying for general distribution, for promotion, for creating new works, or for resale. Specific permission must be obtained in writing from CRC Press LLC for such copying.

Direct all inquiries to CRC Press LLC, 2000 N.W. Corporate Blvd., Boca Raton, Florida 33431.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation, without intent to infringe.

Visit the CRC Press Web site at www.crcpress.com

© 2003 by CRC Press LLC

Lewis Publishers is an imprint of CRC Press LLC

No claim to original U.S. Government works

International Standard Book Number 1-56676-820-9
Library of Congress Card Number 2002041502
Printed in the United States of America 1 2 3 4 5 6 7 8 9 0
Printed on acid-free paper

Dedication

To Padma, Theresa and Bertha, for their understanding

Preface

In the mid-1980s, municipal agencies operating large publicly owned treatment works (POTWs) shared concern and uncertainty about pending amendments to the Clean Air Act. At the crux of the concern were maximum achievable control technology (MACT) regulations for emissions of volatile organic compounds (VOCs) from their facilities. Based on the knowledge — or lack of it — existing at that time, most managers operating POTWs were concerned that they would probably be required to add or redirect their air-quality-related functions to address VOC emissions. This was particularly true for large POTWs in the extremely severe ozone non-attainment areas of the United States.

The shared concern of many POTWs was the driving force behind intense efforts to ensure that undue burden was not imposed on municipal agencies to control a problem that was neither well defined nor understood. An organized group of utility managers, engineering consultants, university researchers and others emerged under the umbrella of the Association of Municipal Sewerage Agencies (AMSA) and this group was committed to providing the tools, concepts, policies and information for POTWs to develop or optimize air quality compliance activities. An impressive body of information has resulted from the collective work of this group as well as from the individual contributions of various municipal agencies and concerned industries. A large amount of pertinent and valid information on the qualitative and quantitative nature of VOCs entering POTWs and the annual rate of their emissions was also generated to determine the extent of the problem related to VOC emissions. This group has committed to providing the tools, concepts, policies and information for POTWs to develop or optimize air quality compliance activities. The science-based concept data developed under the auspices of AMSA were used in cooperative industry efforts with the U.S. Environmental Protection Agency (U.S. EPA) to establish the complexity of air quality compliance at POTWs and to develop realistic regulatory requirements.

The seeds of this book grew from these collaborative efforts. In a desire to create a memento of years of professional camaraderie, the undersigned decided to capture the significant information being generated and preserve it in book form. Thus, this book is a “hands-on” record of a good deal of the information gathered by a number of investigators who collectively collaborated to fill the gaps in the knowledge that existed prior to the promulgation of the MACT standards rules that govern and control the emission of VOCs from POTWs.

We wish to emphasize that this book has been made possible by a number of contributors (listed elsewhere) who have provided key discussions and conceptual input. We also wish to acknowledge the contribution of many others whose work and studies are referenced so frequently in these pages.

We believe that lessons learned from successful air quality compliance programs at existing POTWs are a significant resource. Much good work has been done on VOC emissions from POTWs, particularly in Chicago, Philadelphia, New York and major metropolitan areas in northern and southern California. Our intent was to gather this material so that others could use it. By sharing information and success stories, utilities will not have to "reinvent the wheel," but instead can select practices and procedures that best match their own situations and objectives. The result should be a comprehensive program that includes POTW-specific air emissions inventory information, measurement techniques and viable control options. In addition, we have also made an attempt to provide POTW managers a road-map approach using a critical-mass concept to determine the required number of personnel in terms of full-time equivalents (FTEs) to have a satisfactory air quality compliance program at their facilities.

We are indebted to Ms. Deborah Messina for her untiring efforts and patient disposition in providing her secretarial and wordprocessing skills in assembling the draft chapters and carefully tracking the revisions made. We are also grateful to Ms. Melissa Blanton for serving as the technical editor and providing expert advice and to Ms. Jessica Habetler for providing additional wordprocessing skills.

Prakasam Tata, Ph.D., Q.E.P.
Jay Witherspoon, M.S.
Cecil Lue-Hing, D.Sc., P.E.
Chicago, Illinois

Authors

Prakasam Tata, Ph.D., Q.E.P., recently retired, after 28 years of service, from the Metropolitan Water Reclamation District of Greater Chicago (District) as the Assistant Director of Research and Development. Currently, he is affiliated with the Illinois Institute of Technology, Chicago as a research professor in the Chemical and Environmental Engineering Department and previously taught several graduate level courses. Prior to his retirement, he was responsible for the management of all environmental monitoring and research activities of the District. He has more than 35 years' experience in wastewater treatment, biosolids management, odor and VOC control, animal waste treatment and environmental pollution problems of developing countries.

Dr. Tata, who is a Qualified Environmental Professional (QEP), was active in the Water Environment Federation by serving in leadership roles of various committees. He also served as co-chair of the Air Quality Committee of the Association of Metropolitan Sewerage Agencies. Currently, he is vice-chair of the Board of Editorial Review of the *Water Environment Research Journal*. He also consulted on wastewater treatment and water quality issues with various organizations such as the United Nations Development Program, World Bank, United States Agency for International Development and National Academy of Sciences. He authored, coauthored, or edited four books and published numerous articles and reports. Dr. Tata is the recipient of several awards.

Jay Witherspoon, M.S., a CH2M HILL vice president in the firm's Water Business Group, has more than 22 years of experience in water and wastewater regulatory compliance; biosolids management and odor control; air and odor emissions monitoring, control and compliance; worker health and safety; and emergency and facility security preparedness. He has worked with clients to assist in the planning, design, selection and operation of industrial and municipal systems, directed ongoing applied research studies and designs, written papers and books, served in leadership roles in professional societies, taught university-level classes and been progressively responsible for public- and private-sector engineering, management and administration of projects and programs. He is very active in the Water Environment Federation and the Air and Waste Management Association and is responsible for conducting several training and pre-conference workshops on air emissions and air quality issues.

Mr. Witherspoon's most recent accomplishments include the exploration of the full range of program alternatives and development of systems that enabled clients in California, Washington and the East Coast, Singapore, Australia, New Zealand, Canada and Puerto Rico to successfully comply with federal, state and local regulations. For his professional accomplishments within CH2M HILL, he has been awarded the honor of Fellow, which represents the highest level of capability that is reserved for a select few technologists within the firm.

Cecil Lue-Hing, D.Sc., is the retired Director of Research and Development (R&D) for the Metropolitan Water Reclamation District of Greater Chicago and is currently principal of the Environmental Engineering Consulting firm of Cecil Lue-Hing and Associates Inc., in Chicago. During his 28-year tenure at the District, Dr. Lue-Hing provided R&D direction for the combined sewer overflow, the Tunnel and Reservoir Plan and the Sidestream Elevated Pooled Aeration System in the Chicago River. He established and directed a comprehensive water quality monitoring program for the Greater Chicago Waterway system and the upper Illinois River from Chicago to Peoria. Dr. Lue-Hing played a key role in the restoration of the Chicago River.

Dr. Lue-Hing directed all of the analytical laboratory services, wastewater research, biosolids research, air quality, VOC and odor research programs. He also directed the District's environmental regulatory enforcement program for the control of industrial effluents and the Industrial User Charge Program. He is also nationally recognized as a biosolids management expert, has written extensively and has authored, co-authored or edited two reference texts on biosolids management, two on industrial wastewater control and two on sewage microbiology. Dr. Lue-Hing is a Registered Professional Engineer, a Diplomate of the American Academy of Environmental Engineers and a member of the National Academy of Engineering. In addition, he has received many prestigious professional awards.

Contributors

Thomas R. Card
Environmental Management Consulting
Enumclaw, WA

Ing-Yih Cheng
City of Los Angeles Environmental Monitoring Division
Los Angeles, CA

Richard L. Corsi
University of Texas at Austin
Austin, TX

William Desing
CH2M HILL, Inc.
Milwaukee, WI

Cecil Lue-Hing
Cecil Lue-Hing & Associates
Chicago, IL

Farhana Mohamed
City of Los Angeles Environmental Monitoring Division,
Los Angeles, CA

Hugh Monteith
Enviromega, Inc.
Dundas, ON

David A. Olson
University of Texas at Austin
Austin, TX

Wayne Parker
Carleton University
Ottawa, ON

Albert B. Pincince
Camp, Dresser & McKee
Cambridge, MA

Prakasam Tata
Metropolitan Water Reclamation District of Greater Chicago
Chicago, IL

Jay Witherspoon
CH2M HILL, Inc.
Seattle, WA

Table of Contents

Chapter 1
Introduction..1
Prakasam Tata, Jay Witherspoon and Cecil Lue-Hing

Chapter 2
U.S. Air Quality Regulations 7
Jay Witherspoon, William Desing and Prakasam Tata

Chapter 3
Occurrence of Volatile Organic Compounds in Wastewater..................................37
Prakasam Tata, Tom Card and Cecil Lue-Hing

Chapter 4
Source Characterization and VOCs of Importance..59
Tom Card, Prakasam Tata, Cecil Lue-Hing and Jay Witherspoon

Chapter 5
Unit Processes and Emissions: An Overview..73
Jay Witherspoon, William Desing and Prakasam Tata

Chapter 6
VOC Emissions from Sewers..97
David Olson, Richard Corsi and Prakasam Tata

Chapter 7
VOC Emissions from Preliminary and Primary Treatment.................................117
Al Pincince

Chapter 8
VOC Emissions from Dissolved Air Flotation 127
Hugh Monteith and Wayne Parker

Chapter 9
VOC Emissions from Biological Treatment Systems: Activated Sludge Process..145
Prakasam Tata and Cecil Lue-Hing

Chapter 10
VOC Emissions from Fixed Film Processes..155
Hugh Monteith and Wayne Parker

Chapter 11
VOC Emissions from Biosolids' Dewatering Processes.......................................171
Hugh Monteith and Wayne Parker

Chapter 12
Sampling and Analytical Methods for Hazardous Air Pollutants 189
Farhana Mohamed, Prakasam Tata and Ing-Yih Cheng

Chapter 13
VOC Emission Estimation Methods 227
Prakasam Tata and Jay Witherspoon

Chapter 14
VOC Emissions from Wastewater Treatment Facilities..253
Prakasam Tata, Jay Witherspoon and Cecil Lue-Hing

Chapter 15
Control Technologies..285
Jay Witherspoon, Prakasam Tata, Tom Card and Cecil Lue-Hing

Chapter 16
Control Technology Evaluation...319
Jay Witherspoon and William Desing

Chapter 17
Epilog...335
Jay Witherspoon, Prakasam Tata and Cecil Lue-Hing

Appendix I..361

Appendix II...379

Appendix III..393

Index...399

1 Introduction

Prakasam Tata, Jay Witherspoon and Cecil Lue-Hing

CONTENTS

1.1 Overview 2
1.2 Organization 2
  1.2.1 Background Information 3
  1.2.2 Potential Approaches to Emissions Estimation and Control 4
  1.2.3 Strategic Approaches to Air Quality Compliance 5

The nation's publicly owned treatment works (POTWs) daily address a number of planning, operations, maintenance, management and regulatory compliance issues to provide cost-effective, environmentally sound and technically reliable collection, treatment or disposal of wastewater for their ratepayers. Although most POTW personnel are primarily concerned with the treatment of wastewater and residuals and receiving water quality, POTW managers must also deal with air quality issues relating to emissions of odors, criteria pollutants and volatile organic compounds (VOCs).

This book focuses on air quality compliance challenges, especially the emission of VOCs from POTWs and other air emissions in general. The objective of the book's authors and contributors is to provide the tools, concepts, policies and information for POTWs to develop or optimize air quality compliance activities, particularly with respect to POTW VOC emissions and to assess labor and capital needs to maintain an overall air quality compliance program's long-term viability.

Because even the "best" air quality compliance programs require some fine-tuning and adjustments, this book provides information that can be adapted to a variety of POTW sizes, process trains and system complexities. Air emissions data are presented for most typical POTW processes for use in air emissions inventory and other permitting activities. The book also contains information on how to characterize air emissions, air dispersion modeling and risk assessment methods and much, much more. Readers are encouraged to use this information to assess, plan, develop or refine and implement successful, fully compliant programs, as well as to enter into meaningful, focused discussions with internal program funders on what is or is not needed for a fully compliant program.

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

1.1 OVERVIEW

All states are required to be in compliance with the federal Clean Air Act and an increasingly stringent series of Clean Air Act Amendments (CAAAs). How POTWs demonstrate, document, or show compliance with federal or state or local quality laws and regulations varies significantly from POTW to POTW and from state to state. Compliance is often based on the aggressiveness of the local, state or federal air quality regulatory agency in implementing these laws and regulations and in their enforcement actions and inspections. Another important factor is how proactive the POTW is in meeting regulatory requirements. In the mid-1980s, as potential requirements of the pending CAAA were discussed, an issue of immense concern and uncertainty to municipal agencies operating large POTWs was about how stringent the maximum achievable control technology (MACT) regulations would be for the control of VOCs from their facilities.

The main motivator for this book is the complexity of complying with requirements associated with the emission of VOCs, which occur throughout the wastewater collection, -treatment and solids-handling processes. Other factors, such as emissions of criteria pollutants, e.g., NOx, also affect air quality program compliance. However, prior to the promulgation of the CAAA, addressing VOCs was generally the major driver in whether a POTW achieved compliance.

Based on the knowledge — or the lack of it — that existed in the mid 1980s, most managers operating POTWs felt that they would be required to add or redirect their air-quality-related functions to address VOCs. This was particularly true for POTWs in the extremely severe ozone non-attainment areas of the United States. Intense efforts were made during this time by several major municipal agencies to ensure that undue burden was not imposed on them to control a problem that was not well defined or understood. These efforts were primarily directed at gathering pertinent and valid information on the qualitative and quantitative nature of VOCs entering a POTW and the annual rate of their emissions. This book compiles a good deal of the information gathered by a number of investigators who collectively collaborated to fill the gaps in the knowledge that existed prior to the promulgation of the MACT standards rules that govern and control the emission of VOCs from POTWs.

Many barriers currently prevent optimized air quality compliance from being fully achieved. These include a lack of strict implementation of the promulgated regulations and a lack of financial or human resources. Optimization will rely on specific steps to assess a POTW's needs and current practices, standards and resources and to evaluate those practices, standards and resources with those of other utilities.

1.2 ORGANIZATION

This book contains information compiled by a team of experts who have been working and interacting in the field of air quality research or program management for many years. The combined chapters reflect many views and approaches built on various backgrounds and air quality compliance and assessment experiences. Collectively, these experiences can be used to develop a clear picture — or roadmap

— of how to develop, maintain or build upon a successful air quality compliance program.

The first part of the book provides background information on air emissions requirements and links those requirements to specific wastewater collection and treatment processes. The second part presents practical information on sampling and analytical methods for hazardous air pollutants (HAPs) and on VOC emission estimation methods and control technologies most suitable to POTWs. The final part of the book presents strategic approaches for evaluating emission control technologies and identifies the key elements required in constructing a viable long-term air quality compliance program.

1.2.1 BACKGROUND INFORMATION

Chapter 2, U.S. Air Quality Regulations, sets the regulatory framework within which air quality compliance programs must be developed and implemented. Particular attention is paid to four CAAA regulatory requirements: Title I, Title III, MACT Standards and Title V. Introduced as part of this discussion are important air quality management concepts including National Emission Standards for Hazardous Air Pollutants (NESHAPs), New Source Performance Standards (NSPS) and Risk Management Plans (RMPs). The "major source" definition for VOC emission rates is also described.

To further set the stage for the air quality compliance discussion, Chapter 3 describes the occurrence and identifies the major sources of VOCs in wastewater and discusses the results of various industry efforts to quantify their concentrations. Findings are presented from a range of studies including the United States Environmental Protection Agency (U.S. EPA) 40 City Study, the Research Triangle Institute (RTI) Study and studies conducted in Ontario, Canada; Oakland, California (East Bay Municipal Utility District [EBMUD]); the Association of Metropolitan Sewerage Agencies (AMSA); and New York City.

Chapter 4, Source Characterization and VOCs of Importance, presents an overview of POTW processes and describes a recommended classification strategy for VOCs. A brief review is provided of three major programs being conducted in California, including a VOC characterization and control guidance document for POTWs developed by Tri-TAC, the Joint Emissions Inventory Program (JEIP) and the Pooled Emissions Estimation Program (PEEP). Other characterization data are also discussed.

An overview of POTW unit processes and emissions is presented in Chapter 5. Major components described are collection systems, preliminary/primary treatment, biological treatment, post-biological treatment, solids handling and combustion processes. For each component, a process description is provided, emission mechanisms are described and key factors affecting emissions are discussed. Chapter 5 also describes ways to measure emissions and presents a brief description of the three fate models most widely used for this purpose. These models are WATER7/8/9, the U.S. EPA's public domain model and two proprietary models: the Bay Area Sewage Toxic Emissions (BASTE) model and the Toxic Chemical Modeling Program for Water Pollution Control (TOXCHEM).

Chapters 6 through 11 provide more detailed information on VOC emissions from various unit processes considered to be important emission sources. These are:

- Sewers (Chapter 6)
- Preliminary and primary treatment (Chapter 7)
- Dissolved air flotation (Chapter 8)
- Biological systems/activated sludge (Chapter 9)
- Fixed film process (Chapter 10)
- Biosolids/dewatering (Chapter 11)

Each chapter provides a process description and presents results of recent modeling analyses or other studies.

1.2.2 POTENTIAL APPROACHES TO EMISSIONS ESTIMATION AND CONTROL

Sampling and Analytical Methods for HAPs are the focus of Chapter 12. This chapter describes:

- Sampling methodologies for liquids, solids, ambient air and combustion sources
- Analytical methodologies available to POTWs
- Quality assurance considerations
- Analytical procedures and calibration frequencies
- Method detection limits and reporting levels

Chapter 12 also discusses regulations established by California's South Coast Air Quality Management District (SCAQMD) relating to emission inventories and emission estimated for risk assessments. In addition, Chapter 12 describes the move by the U.S. EPA toward a performance based monitoring system (PBMS) in recognition of difficulties posed by the fact that advances in analytical measurement technology have moved forward more quickly than regulatory requirements for detection levels.

Chapter 13, VOC Emission Estimation Methods, describes in detail the different methods available for POTWs to determine VOC emissions from collection systems and unit processes. These methods are based on approaches such as mass balance, derivation of emission factors, modeling and tracing techniques. Examples of ways to derive concentration-based emission factors — which are related to the influent loading of the individual treatment process — are provided through discussions of the PEEP, JEIP and Tri-TAC programs conducted in California.

Chapter 14, VOC Emissions from Wastewater Treatment Facilities, discusses the quantitation of VOC emissions from the unit processes of wastewater treatment facilities by using emission factors and results of VOC emissions reported by a few major municipal agencies based on general fate model methodology. A comparison is then made of emission estimates and directly measured emission rates. The wide range of emission rate values predicted by the general fate models suggests that the use of models to characterize a plant as a major source using the CAAA 1990 Title

III definition is not reliable. Models, however, can be used for screening purposes. Furthermore, due to the highly conservative nature of the models, if the annual emission rates of POTWs computed by the models are less than the limits specified for major sources, it is safe to assume that the POTWs are not major sources.

Several technologies are potentially available to control emissions from POTWs. Chapter 15, Control Technologies, divides these technologies into five basic categories: traditional vapor phase controls, nontraditional vapor phase controls, containment, process and practice modifications and source control. The applicability of these technologies in controlling VOC emissions from POTWs varies. Chapter 15 focuses on thermal treatment, incinerators, flares, recuperative oxidizers, regenerative oxidizers, catalytic incineration, wet scrubbing, packed-tower scrubbers, mist scrubbers, dry chemical scrubbing, carbon adsorption and biofiltration. General descriptions are provided for these technologies, and factors such as removal efficiency, potential operating problems and cross-media impacts are discussed. Costs developed through studies and reported in the literature are also provided. The information presented in this chapter can be used as part of the cost effectiveness evaluation required when a control technology such as best available control technology (BACT) must be applied.

1.2.3 STRATEGIC APPROACHES TO AIR QUALITY COMPLIANCE

Chapter 16, Control Technology Evaluation, reviews the evaluations that may be required for CAAA compliance if emissions exceed certain thresholds. Traditional air emission control approaches are often ineffective at POTWs, where air emissions are generally characterized by low concentrations, high volumes and multiple sources. In recognition of the unique characteristics of POTWs, Chapter 16 presents a control technology evaluation approach that incorporates two regulatory concepts: the U.S. EPA Top-Down BACT procedure and the incremental emission (risk reduction) procedure. The suggested methodology, comprising six sequential steps, can be used to select control measures designed to meet a wide variety of requirements.

Chapter 17, Conclusions, provides the key elements to build a compliant air quality program. Using information developed in Chapters 2 through 16, Chapter 17 summarizes major factors affecting VOC emissions and presents a roadmap approach for VOC emissions control. Nine major air quality control program elements are described. Recommended allocation of specific tasks for each program element are presented by full-time equivalents (FTEs), based on a POTW of approximately 50 mgd. Ways to scale up or scale down FTE allocations are then suggested for POTWs ranging from 1 mgd to 1 billion gallons a day. Through the roadmap approach, POTWs can select the air quality program compliance strategies that best meet their site-specific needs.

2 U.S. Air Quality Regulations

Jay Witherspoon, William Desing and Prakasam Tata

CONTENTS

2.1 Introduction 8
2.2 Title I: Provisions for Attainment and Maintenance of National Ambient Air Quality Standards 10
  2.2.1 Reasonably Available Control Technology (RACT) 12
  2.2.2 Prevention of Significant Deterioration (PSD) 12
  2.2.3 PSD Applicability 13
  2.2.4 New Source Review (NSR) and Permitting in Non-Attainment Areas 15
  2.2.5 New Source Performance Standards (NSPS) 15
2.3 Title III: Hazardous Air Pollutants (HAPs) 18
2.4 POTW MACT Standards 18
  2.4.1 Residual Risk Analysis 25
  2.4.2 Accidental Release and Prevention Program (Risk Management Plans) 25
    2.4.2.1 Applicability of RMP and PSM 25
    2.4.2.2 Requirements of RMP and PSM 26
    2.4.2.3 Hazard Assessment/Offsite Consequence Analysis 27
    2.4.2.4 Prevention Program 27
    2.4.2.5 Emergency Response Program 28
    2.4.2.6 RMP and PSM Approach 28
      2.4.2.6.1 Decreasing Material Inventory 28
      2.4.2.6.2 Use Refined Modeling to Minimize Distance in Offsite Consequence Analysis 29
      2.4.2.6.3 Select Appropriate Method for the PHA 30
2.5 Title V: Operating Permits 30
  2.5.1 Applicability 30
  2.5.2 Federally Enforceable State Operating Permits (FESOPs) or Synthetic Minor 32

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

2.5.3 Alternate Operating Scenarios 32
2.6 National Air Toxics Program: The Integrated Urban Strategy 33
2.7 Other Regulations 34
2.8 Summary 35

2.1 INTRODUCTION

Air quality regulation in the United States began on a federal level in 1955 with the passage of the Air Pollution Control Act. This program was replaced with the Clean Air Act of 1963, which for the first time started to address interstate air pollution problems. The Clean Air Act Amendments (CAAA) of 1966 extended the 1963 Act and provided grants-in-aid to state and local air pollution programs. The CAAA of 1970, along with the creation of the United States Environmental Protection Agency (EPA), gave impetus to the air quality regulations.

Amendments passed in 1970 established for the first time national ambient air quality standards (NAAQS) and required State Implementation Plans (SIPs) and a timetable for achieving the standards by 1973. The 1970 CAAA also authorized the Public Health Survey of the Department of Health Education and Welfare to establish emission standards for all sources for certain hazardous air pollutants (HAPs) (e.g., asbestos, beryllium, mercury and vinyl chloride). These are called the National Emission Standards for Hazardous Air Pollutants (NESHAPs). These amendments also set automobile emission standards for 1975 cars and aircraft engines.

The CAAA of 1977 made significant modifications and additions to the 1970 Act, including specifying of new source performance standards (NSPS), establishing three classes of air quality regions — Class I (pristine areas), Class III (industrial areas), Class II (almost all other areas) and specifying provisions to prevent significant deterioration of these regions with acceptable air quality and provisions to bring areas not in attainment with standards into attainment. This act also created a formal technical prevention of significant deterioration (PSD) procedure to be followed and the results submitted to the regulatory agency by any sources seeking a permit to show that any changes in air quality will be consistent with the classifications.

Additional CAAAs were passed in 1990. The new amendments meant more stringent air emissions controls, increasingly complex monitoring, data collection and reporting, and significant emission source permitting and compliance requirements for a variety of emissions sources. For the first time, the CAAA specifically focused on POTWs. Prior to this point, POTWs were regulated and are still regulated, primarily under state or local air quality laws and regulations stemming from the Clean Air Act. The intent of the 1990 amendments was to increase protection of the public from three major areas of air pollution: acid rain, urban air pollution and HAPs. The 1990 CAAA specified detailed inventorying, reporting and compliance requirements for these pollutants.

Table 2.1 summarizes the major provisions of the 1990 CAAA, which are divided into 11 titles. Titles I, III and V are anticipated to have potential significant implact on POTWs and are described in more detail below.

TABLE 2.1
Provisions of 1990 CAAA

Title	Key Provisions
Title I: Provisions for Attainment and Maintenance of National Ambient Air Quality Standards	Classifies major urban areas according to the level of non-attainment of ozone, carbon monoxide (CO), lead, sulfur oxides (SOx), nitrogen oxides (NOx) and particulate ambient air quality standards under this title. Primary focus is on combustion and combustion byproduct emissions.
Title II: Provisions Relating to Mobile Sources	Focuses on controlling the emission of compounds such as VOCs, CO and NOx. Requires reduction at prescribed levels in a timely manner for a variety of sources including cars, trucks and non-road engines.
Title III: Hazardous Air Pollutants	Provides regulations to control emissions of 188 HAPs, including VOCs, semivolatile organic compounds and workplace toxins. Requires "major sources" of HAPs emissions to apply for a Title V permit. Regulates commonly used disinfection chemicals such as ammonia, chlorine gas and sulfur dioxides.
Title IV: Acid Deposition Control	Deals primarily with the control of emission of NOx and SOx.
Title V: Permits	Requires all current major sources under Title I, Title III and Title IV to obtain a permit.
Title VI: Stratospheric Ozone and Global Climate Protection	Controls and regulates chemicals that deplete the ozone layer of the stratosphere.
Title VII: Provisions Relating to Enforcement	Discusses penalties for noncompliance and contains provisions for citizens to seek penalties against violators.
Title VIII: Miscellaneous Provisions	Addresses federal grants, technical and management studies and report submittal.
Title IX: Clean Air Research	Covers research areas including monitoring, modeling, environmental health effects, pollution prevention and acid rain research and assessment.
Title X: Disadvantaged Business Concerns	Addresses disadvantaged businesses.
Title XI: Clean Air Employment Transition Assistance	Contains provisions for providing unemployment benefits through job training, etc., for workers displaced as a result of 1990 CAAA compliance.

2.2 TITLE I: PROVISIONS FOR ATTAINMENT AND MAINTENANCE OF NATIONAL AMBIENT AIR QUALITY STANDARDS

Title I, Provisions for Attainment and Maintenance of National Ambient Air Quality Standards, establishes NAAQS for six criteria pollutants. These are the same pollutants originally listed in the 1970 CAAA, namely, ozone, CO, NO_x, SO_x, particulate matter (PM_{10}) and lead. Two standards are established for each criteria pollutant: a primary standard based on protecting public health and a secondary standard designed to protect public welfare. A list of the NAAQS concentration value and averaging period for each criteria pollutant established in the 1990 CAAA is provided in Table 2.2.

In addition to these standards, new NAAQS were promulgated for ozone and $PM_{2.5}$ (particulate matter of 2.5 microns [μ] in size) in 1997. The 1997 NAAQS concentration and averaging periods for ozone and $PM_{2.5}$ are provided in Table 2.3. At the time of this book's publication (2003) , these standards were under judicial review.

Determination of ozone attainment status for the 1-h NAAQS involves using a rolling 3-year time period. For example, if during any three consecutive years 1-h average ozone concentrations exceed 0.12 parts per million by volume (ppmv) four times, the area is designated as non-attainment. The value of the fourth highest measured ozone concentration is used as the ozone design value. In addition to the attainment/non-attainment classification system, ozone non-attainment regions are classified as being either marginal, moderate, serious, severe or extreme; the classification depends on the extent to which their ozone design value exceeded the ozone NAAQSs, or the number of times per year that they exceeded the NAAQSs. Design values for each of the five designations are provided in Table 2.4. The status of attainment areas can change and the POTW should contact the state or local regulatory agency to determine the area's attainment status.

TABLE 2.2
National Ambient Air Quality Standards (NAAQS)

Criteria Pollutant	Primary Standard Concentration	Averaging Period	Secondary Standard Concentration	Averaging Period
Ozone	0.12 ppmv	1 h	0.12 ppmv	1 h
Carbon monoxide	9 ppmv	8 h	9 ppmv	8 h
	35 ppmv	1 h	35 ppmv	1 h
Nitrogen dioxide	0.053 ppmv	Annual	0.053 ppmv	Annual
Sulfur dioxide	0.03 ppmv	Annual	0.5 ppmv	3 h
	0.14 ppmv	24 h		
Particulate matter (PM_{10})	50 $\mu g/m^3$	Annual	50 $\mu g/m^3$	Annual
	150 $\mu g/m^3$	24 h	150 $\mu g/m^3$	24 h
Lead	1.5 $\mu g/m^3$	Calendar quarter	1.5 $\mu g/m^3$	Calendar quarter

Source: http://www.epa.gov/airs/criteria.html

TABLE 2.3
Proposed Changes to NAAQS

Criteria Pollutant	Primary Standard Concentration	Averaging Period	Secondary Standard Concentration	Averaging Period
Ozone	0.08 ppmv	8 h	0.08 ppmv	8 h
Particulate matter ($PM_{2.5}$)	15 μg/m^3	Annual	15 μg/m^3	Annual
	65 μg/m^3	24 h	μg/m^3	24 h

Source: http://www.epa.gov/ttn/oarpg/naaqsfin/naaqsfac.html

TABLE 2.4
Ozone Non-Attainment Area Requirements

Designation	Ozone Design Value (ppmv)	Title I Major Source Threshold Triggers for VOCs or NO_X Potential Emissions (Tons/year)	Attainment Deadline
Marginal	0.121–0.137	100	November 15, 1993
Moderate	0.138–0.159	100	November 15, 1996
Serious	0.160–0.179	50	November 15, 1999
Severe	0.180–0.190	25	November 15, 2005
	0.191–0.279		November 15, 2007
Extreme	> 0.280	10	November 15, 2010

Source: Clean Air Act Amendments 1990 (http://www.epa.gov.air/oaq_caa.html.

Once designated as ozone non-attainment, the agency responsible for air quality within the designated area is required to devise and implement an air quality plan that will bring the area back into compliance with the ozone NAAQS. This plan, commonly referred to as an SIP, is submitted to the EPA for approval, and documents existing conditions, source control strategies to be implemented (both quantity and timeframe for reductions) and resulting benefits that these strategies will have on ozone concentrations.

Ozone is a secondary pollutant, i.e., it is not emitted directly, but is formed in the atmosphere as a result of photochemical reactions involving sunlight. Thus, VOCs and NOx control strategies revolve around reduction of the two major precursors:VOCs and NOx. To facilitate developing effective control strategies, area-wide emissions inventories are required and include emissions generated from point (large stationary sources, e.g., utilities), area (small stationary sources, e.g., gasoline service stations), mobile (on- and off-road vehicles) and biogenic sources. Classification as a major source of emissions in an ozone non-attainment area depends on the non-attainment status. Major source classification triggers are provided in Table 2.4. The trigger levels are potential emissions, not actual emissions. Potential emissions assumes the source is operated continuously at its maximum rated capacity and takes into account physical limitations, federally enforced limits (e.g., permit conditions that are approved by SIPs) and emissions control technology. Several different definitions are used for major source in different titles of the Clean Air Act. Non-attainment designations and their originally proposed attainment schedule are provided in Table 2.4. Many areas have not or will not meet the attainment deadline; as a result, agencies could make emission controls more stringent in an attempt to make such areas reach attainment status.

2.2.1 Reasonably Available Control Technology (RACT)

The 1977 CAAA require that existing sources in non-attainment areas install reasonably available control technology (RACT) as expeditiously as practicable. Activities often require existing sources to be retrofitted with new treatment equipment or modified to meet RACT requirements. RACT is an evolving standard; it is determined on a case-by-case basis by the state, taking into account the economic and technical circumstances surrounding the sources being regulated. RACT is generally considered a less stringent level of control than those required by other parts of the Clean Air Act. The number and types of sources that must apply RACT varies with the intensity of the non-attainment problem and the states' rules and guidelines. The state or local air regulators should be consulted to determine whether RACT is applicable to an existing major source in a non-attainment area.

2.2.2 Prevention of Significant Deterioration (PSD)

To ensure that areas currently in attainment with NAAQS do not slip into non-attainment status, the EPA created PSD guidelines. Before the CAAA of 1977, it was theoretically possible to pollute clean air up to the limits of the ambient standards simply by locating more industry in clean air regions. The PSD guidelines placed incremental limits on the amount of ambient air quality deterioration allowed resulting from construction of a new major source or reconstruction of an existing major source of pollution. The PSD rules defined Class I, Class II and Class III areas. The ambient concentrations would be allowed to be almost nothing in Class I areas, by specified amounts in Class II areas and by larger amounts in Class III areas. The PSD program requires a rigorous preconstruction review process for any new or modified source to ensure that air quality is not degraded beyond increments above a baseline of existing ambient concentrations of criteria pollutants. The need to perform a PSD preconstruction review should be identified early because the process can take up to 12 to 18 months and the permit must be approved before construction can begin. Therefore, if the need for a PSD preconstruction permit is not identified early, then PSD permit preparation could be on the project's critical path and extend the time required to install the new source.

If a source considered major under PSD rules proposes to construct new emission sources that will increase its (the source's) overall emissions beyond certain thresholds, then the source must carry out the following before being allowed to start construction:

Perform ambient monitoring of existing air quality. This typically involves installing equipment that automatically and continuously samples and analyzes the air for criteria pollutants at several locations surrounding the source. Normally, the state's monitoring network and data can be used.

- Determine the impacts that the proposed source would have on the ambient air quality. This is almost always accomplished using computer modeling that can predict how the emissions will be dispersed under different atmospheric conditions.
- Assess the source's impact on soils, vegetation and visibility, as well as the air quality impacts that would directly result from growth associated with the source or modification.
- Demonstrate that emissions from the facility will not violate the PSD ambient air quality concentration increments.
- Apply the best available control technology (BACT). BACT is an emission limit based on the "maximum degree of reduction of each pollutant subject to regulation which is achievable." BACT is determined on a case-by-case basis by the permitting authority and takes into account energy, environmental and economic costs. BACT is usually a more stringent method of control than that required under RACT and is applied to new or modified emission sources.

For sources that have federally mandated NSPS such as 40 Code of Federal Regulations (CFR) 60 NSPS Subpart O; sewage treatment plant incinerators, BACT is required to be at least as stringent as NSPS. For sources without NSPS, BACT is determined on a case-by-case basis. NSPS is explained in more detail below.

2.2.3 PSD Applicability

If a source considered major under PSD rules proposes to modify or construct new emission sources that will increase the source's overall emissions beyond certain thresholds, then the source must apply for and receive a PSD permit before being allowed to begin construction of the new source. A source is defined as a major source for PSD applicability if:

- It is one of 28 regulated source categories and potential emissions of any single pollutant regulated under the Clean Air Act exceed 100 tons per year. POTWs are not one of the 28 source categories and are therefore not subject to the 100-ton-per-year threshold.
- It is not one of the 28 regulated sources and has the potential to emit more than 250 tons per year of any single regulated pollutant. This threshold is applicable to POTWs located in attainment areas. See the subsequent discussion for POTWs located in non-attainment areas.

Fugitive emissions are not required to be considered in calculating the emissions to compare to the 250-ton-per-year threshold in an attainment area. Fugitive emissions are defined as emissions that cannot reasonably be vented through a stack or chimney. For POTWs, depending on size, emissions from open tanks such as clarifiers and aeration basins are usually considered fugitive because these emissions are not easily contained and vented. An existing major source that undergoes a major modification is required to apply for a PSD permit before construction can begin. A modification is major if the emissions exceed the significance levels for regulated pollutants. These significant emission levels are shown in Table 2.5. If a source exceeds 250 tons per year for a single pollutant in an attainment area and a modification is made in which emissions exceed the significance level for a second different pollutant, then the source must still comply with all PSD permitting requirements for the second pollutant. Any source located within 10 kilometers of a pristine Class I area may be significant and require a PSD permit. Any PSD source within 100 kilometers of a Class I area must have its application reviewed by the Class I area's federal land manager, usually the National Park Service or Fish and Wildlife Service.

To determine the amount of emissions increase to be compared with the significance levels shown in Table 2.5, the net emissions increase must be determined. The net emissions increase is defined as: Net emissions increase = proposed increase in emissions – source-wide creditable decreases + source-wide creditable increases

The proposed increase in emissions is defined as:

Proposed increase in emissions =
proposed allowable emissions – current actual emissions.

The current actual emission rate is defined as the most recent 2-year average emission rate. Because the proposed allowable emissions are often significantly greater than the current actual emissions, the significance level can easily be exceeded unless reductions in emissions from other sources are made. The source-wide creditable decreases must be federally enforceable decreases, which usually

TABLE 2.5
Significant Emission Rates for PSD Applicability

Pollutant	Emission Rate (tons/yr)	Pollutant[a]	Emission Rate (tons/yr)
CO	100	Asbestos	0.007
NO_X	40	Mercury	0.1
PM	25	Beryllium	0.0004
PM_{10}	15	Fluorides	3
SO_2	40	Vinyl Chloride	1
VOCs	40	H_2SO_4	10
Lead	0.6	Total Reduced Sulfur Compounds	10

Source: 40 CFR, Part 51 and 52, 1996

[a] These are now moved to Title III as part of the Title III, Section 112 HAPs program.

means that the decreases are documented as a permit condition. Because significance levels can be triggered, sources in an attainment area will often attempt to limit overall potential emissions to less than the 250 tons per year major source level to avoid being subject to PSD permitting. The emission increases are contemporaneous, which is defined by the PSD regulations as occurring within five years prior to the construction of the modification; this prevents sources from avoiding the PSD rules by adding several small sources over a relatively short period of time. Figure 2.1 graphically presents an example of how to determine the contemporaneous emission decreases for switching a boiler from fuel oil to natural gas.

2.2.4 New Source Review and Permitting in Non-attainment Areas

The process for obtaining a permit to construct a new or modified source in a non-attainment area is similar to that for obtaining a PSD permit in an attainment area. However. the emission thresholds that require a permit are lower and control technology requirements more stringent to bring the area back into attainment with air quality standards. The level of emission increases that trigger the need for a new source review permit are lower for those pollutants with which the area is not in attainment; for other attainment pollutants, the trigger levels are the same.

For new sources in non-attainment areas, the source must comply with the lowest achievable emission rate (LAER), which is considered the most stringent performance standard under the CAA and cannot be any less stringent than any applicable NSPS. Essentially, LAER requires that the most stringent level of control specified in any SIP or by any source in the same or similar source category must be implemented. For example, because air quality in the Los Angeles, California area is one of the worst in the country, the emission control requirements set by the regulating agency in that area, the South Coast Air Quality Management District (SCAQMD), are the most stringent. Therefore, the SQAQMD standards are often required to be applied as LAER in non-attainment areas.

New or modified sources in non-attainment areas must obtain offsetting emission reductions, such that the increases in emissions from the new or modified source are offset by an equal or greater reduction in actual emissions from the same or other sources in the area. The amount of the offset required depends on the severity of the non-attainment condition involved. Examples of the level of offsets required are shown in Table 2.6. These offsets can be obtained through either reducing emissions from other existing sources or by using or purchasing previously banked emissions reductions. Emissions reduction offsets can be obtained by reducing emissions from another source in the same facility by installing controls that exceed regulatory requirements. In several states, it is possible to buy and sell emissions offsets in a trading system similar to existing commodities markets.

2.2.5 New Source Performance Standards (NSPS)

As part of the CAAA of 1970, specific emission standards were established for categories of new sources which could contribute significantly to air pollution. EPA

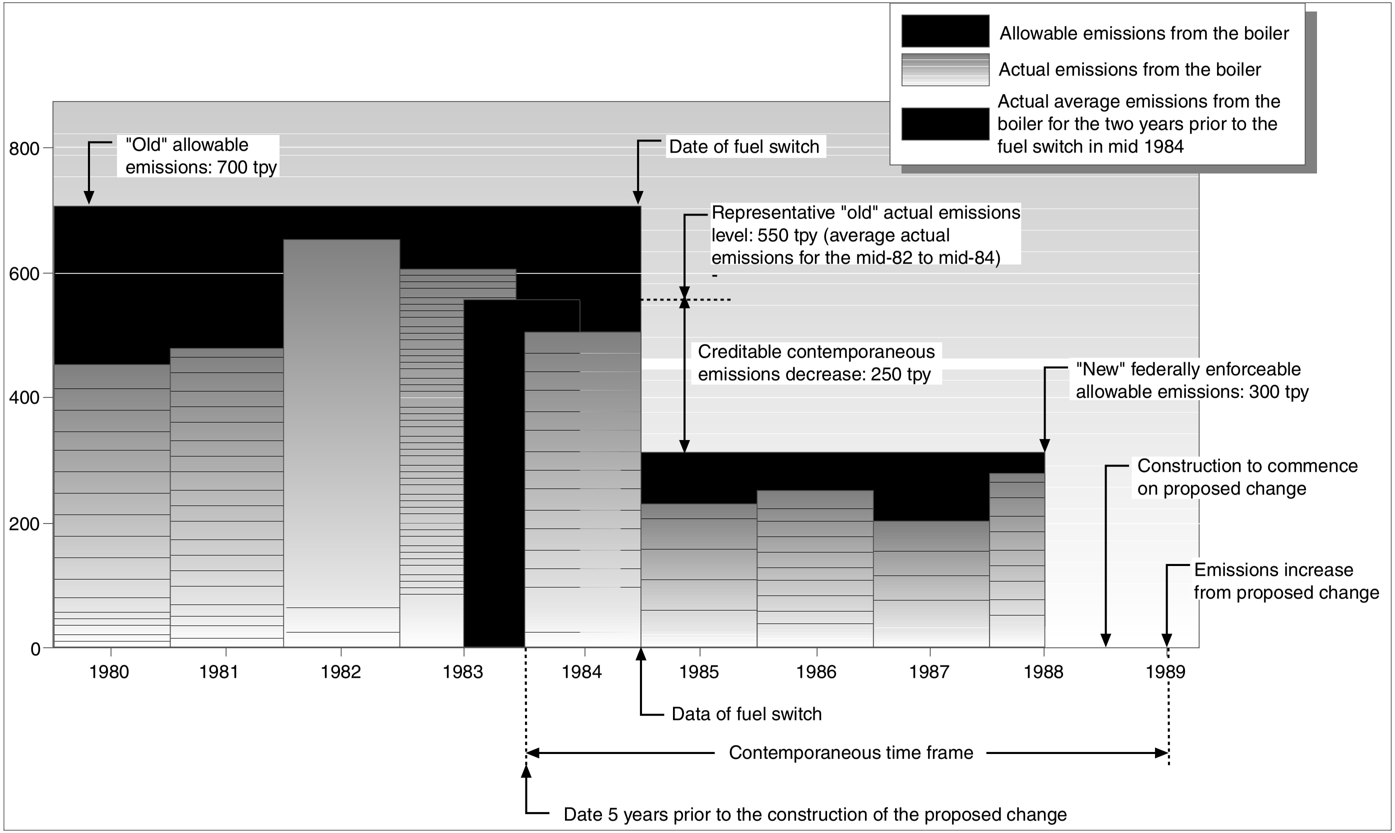


FIGURE 2.1 Example of PSD applicability.

TABLE 2.6
Ozone Non-Attainment Area Offset Requirements

Pollutant[a]	Designation	Offset Ratio	Major Source Trigger (tpy)
VOC/NO_X	Marginal	1.10:1	100
VOC/NO_X	Moderate	1.15:1	100
VOC/NO_X	Serious	1.20:1	50
VOC/NO_X	Severe	1.30:1	25
		1.30:1	25
VOC/NO_X	Extreme	1.50:1	10

[a] Under CAA Section 182 (f), EPA may exempt certain major NOx sources where NOx reductions would "not contribute to attainment of the national ambient air quality standard in the area." Also, major source threshold applies to VOC or NOx emissions, not combined emissions.

is required to periodically revise the NSPS list of regulated sources and publish standards reflecting "the degree of emission reduction achievable through application of the best system of emission reduction" taking into account cost, non-air impacts and energy requirements. The purpose of NSPS is to prevent the deterioration of air quality from new sources and to take advantage of the economies of building pollution control into the design of new sources rather than retrofitting existing sources. The NSPS require specific limitations on pollutants from regulated sources. For example, the NSPS for biosolids incinerators includes a requirement that does not allow particulate emissions to exceed 1.3 pounds per dry ton of biosolids. Table 2.7 shows some of the common sources found at POTWs that may be regulated under NSPS.

TABLE 2.7
Sources Commonly Found at POTWs that May Be Subjected to New Source Performance Standards

NSPS Regulation	Source	Date for Compliance[a]
40 CFR 60 Subpart 0	Biosolids incinerators	June 11, 1973
40 CFR 60 Subpart Dc	Boilers rated between 10 MMBTU/hr and 100 MMBTU/hr	June 9, 1989
40 CFR 60 Subpart GG	Stationary gas turbines with input of at least 10.7 gigajoules per h	October 3, 1977

[a] Sources that commence construction, reconstruction or modification after this date must comply with the NSPS requirements.

2.3 TITLE III: HAZARDOUS AIR POLLUTANTS

Title III of the 1990 CAAA completely rewrote the existing hazardous air pollutant emission program. The previous program, known as NESHAPS, issued standards over a 20-year period for only eight pollutants. Title III shifted the focus from a pollutant-by-pollutant regulation to a technology-based regulation of source categories.

Title III established a list of 189 HAPs to be regulated (see Table 2.8). This list was subsequently reduced to 188 by deleting hydrogen sulfide. Inclusion of specific chemicals on the list was based on information regarding carcinogenic, mutagenic or reproductive toxicity. In addition to the list of targeted HAPs, source categories were identified for potential HAP emissions control, one of which was POTWs.

To be considered a major source for Title III applicability determination, a facility must have the potential to emit, considering controls, more than 10 tons per year of any single HAP or more than 25 tons per year of total HAPs. If either of these limits is exceeded, the major source is required to comply with maximum achievable control technology (MACT). MACT standards are category-specific by source. For existing sources, the standard requires that controls must be not less stringent than the average emission limitations achieved by the top 12% of the existing sources. For new sources, MACT requires application of controls not less stringent than the best-performing existing similar source.

Emission estimates of HAPs from several POTWs in the United States have shown that most POTWs are not major sources of HAPs. For example, the 1.2 billion gallons-per-day Stickney Water Reclamation Plant in Stickney, Illinois is not a major HAP source despite being one of the largest POTWs in the United States. However, a POTW load that originates from an industry or industries that discharge wastewater containing a large amount of HAPs can volatilize as emissions from POTW unit processes during wastewater treatment. These industries would likely have little or no waste pretreatment prior to discharge to the POTW. Another exception would be a POTW that has high metal or VOC concentrations in its influent, incinerates its biosolids or has a lower incinerator emission control efficiency. Some emission estimation computer models have been shown to be too conservative, causing emission estimates from some POTWs to incorrectly trigger the HAP major source limit. Several of the models and emission factors that are used to estimate HAPs will be presented and discussed elsewhere in this book.

2.4 POTW MACT STANDARDS

On October 26, 1999, EPA promulgated the final MACT rule for POTWs. (*Federal Register*, Vol. 64, No. 206, 57572-57585). The final MACT rule is designed to control HAP emissions from POTWs and does not include collection systems in either major source status applicability determinations or in emission control requirements.

In developing the final rule, EPA created two POTW subgroups: industrial and non-industrial. Industrial POTWs are defined in 40 CFR 63.1595 as follows: "Industrial POTW means a POTW that accepts a waste stream regulated by an industrial NESHAP and provides treatment and controls as an agent for the industrial discharger. The industrial discharger complies with its NESHAP by using the treatment

TABLE 2.8
1990 CAAA Air Toxics List

CAS Number/Chemical Name	CAS Number/Chemical Name	CAS Number/Chemical Name	CAS Number/Chemical Name	CAS Number/Chemical Name	CAS Number/Chemical Name
75070 Acetaldehyde	334883 Diazomethane	50000 Formaldehyde	56382 Parathion	79345 1,1,2,2-Tetrachloroethane	95476 o-Xylenes
60355 Acetamide	132649 Dibenzofurans	76448 Heptachlor	82688 Pentachloronitrobenzene (Quintobenzene)	127184 Tetrachloroethylene (Perchloroethylene)	108383 m-Xylenes
75058 Acetonitrile	96128 1,2-Dibromo-3-chloropropane	118741 Hexachlorobenzene	87865 Pentachlorophenol	7550450 Titanium tetrachloride	106423 p-Xylenes
98862 Acetophenone	84742 Dibutylphthalate	87683 Hexachlorobutadiene	108952 Phenol	108883 Toluene	0 Antimony Compounds
53963 2-Acetylaminofluorene	106467 1,4-Dichlorobenzene(p)	77474 Hexachlorocyclopentadiene	106503 p-Phenylenediamine	95807 2,4-Toluene diamine	0 Arsenic Compounds (inorganic including arsine)
107028 Acrolein	91941 3,3-Dichlorobenzidene	67721 Hexachloroethane	75445 Phosgene	584849 2,4-Toluene diisocyanate	0 Beryllium Compounds
79061 Acrylamide	111444 Dichloroethyl ether (Bis(2-chloroethyl)ether)	822060 Hexamethylene-1,6-diisocyanate	7803512 Phosphine	95534 o-Toluidine	0 Cadmium Compounds
79107 Acrylic acid	542756 1,3-Dichloropropene	680319 Hexamethylphosphoramide	7723140 Phosphorus	8001352 Toxaphene (chlorinated camphene)	0 Chromium Compounds
107131 Acrylonitrile	62737 Dichlorvos	110543 Hexane	85449 Phthalic anhydride	120821 1,2,4-Trichlorobenzene	0 Cobalt Compounds

TABLE 2.8 (CONTINUED)
1990 CAAA Air Toxics List

CAS Number/Chemical Name	CAS Number/Chemical Name	CAS Number/Chemical Name	CAS Number/Chemical Name	CAS Number/Chemical Name	CAS Number/Chemical Name
107051 Allyl chloride	111422 Diethanolamine	302012 Hydrazine	1336363 Polychlorinated biphenyls (Aroclors)	79005 1,1,2-Trichloroethane	0 Coke Oven Emissions
92671 4-Aminobiphenyl	121697 N,N-Diethyl aniline (N,N-Dimethylaniline)	7647010 Hydrochloric acid	1120714 1,3-Propane sultone	79016 Trichloroethylene	0 Cyanide Compounds [a]
62533 Aniline	64675 Diethyl sulfate	7664393 Hydrogen fluoride (Hydrofluoric acid)	57578 beta-Propiolactone	95954 2,4,5-Trichlorophenol	0 Glycol ethers[b]
90040 o-Anisidine	119904 3,3-Dimethoxybenzidine	123319 Hydroquinone	123386 Propionaldehyde	88062 2,4,6-Trichlorophenol	0 Lead Compounds
1332214 Asbestos	60117 Dimethyl aminoazobenzene	78591 Isophorone	114261 Propoxur (Baygon)	121448 Triethylamine	0 Manganese Compounds
71432 Benzene (including benzene from gasoline)	119937 3,3-Dimethyl benzidine	58899 Lindane (all isomers)	78875 Propylene dichloride (1,2-Dichloropropane)	1582098 Trifluralin	0 Mercury Compounds
92875 Benzidine	79447 Dimethyl carbamoyl chloride	108316 Maleic anhydride	75569 Propylene oxide	540841 2,2,4-Trimethylpentane	0 Fine mineral fibers[c]
98077 Benzotrichloride	68122 Dimethyl formamide	67561 Methanol	75558 1,2-Propylenimine (2-Methyl aziridine)	108054 Vinyl acetate	0 Nickel Compounds
100447 Benzyl chloride	57147 1,1-Dimethyl hydrazine	72435 Methoxychlor	91225 Quinoline	593602 Vinyl bromide	0 Polycylic Organic Matter

92524 Biphenyl
117817 Bis(2-ethylhexyl)phthalate (DEHP)
542881 Bis(chloro-methyl)ether
75252 Bromoform
106990 1,3-Butadiene
156627 Calcium cyanamide
105602 Caprolactam
133062 Captan
63252 Carbaryl
75150 Carbon disulfide
56235 Carbon tetrachloride
463581 Carbonyl sulfide
120809 Catechol
131113 Dimethyl phthalate
77781 Dimethyl sulfate
534521 4,6-Dinitro-o-cresol and salts
51285 2,4-Dinitrophenol
121142 2,4-Dinitrotoluene
123911 1,4-Dioxane (1,4-Diethyleneoxide)
122667 1,2-Diphenylhydrazine
106898 Epichlorohydrin (l-Chloro-2,3-epoxypropane)
106887 1,2-Epoxybutane
140885 Ethyl acrylate
100414 Ethyl benzene
51796 Ethyl carbamate (Urethane)
75003 Ethyl chloride (Chloroethane)
74839 Methyl bromide (Bromomethane)
74873 Methyl chloride (Chloromethane)
71556 Methyl chloroform (1,1,1-Trichloroethane)
78933 Methyl ethyl ketone (2-Butanone)
60344 Methyl hydrazine
74884 Methyl iodide (Iodomethane)
108101 Methyl isobutyl ketone (Hexone)
624839 Methyl isocyanate
80626 Methyl methacrylate
1634044 Methyl tert butyl ether
101144 4,4-Methylene bis(2-chloroaniline)
75092 Methylene chloride (Dichloromethane)
101688 Methylene diphenyl diisocyanate (MDI)
106514 Quinone
100425 Styrene
96093 Styrene oxide
1746016 2,3,7,8-Tetra-chloro-dibenzo-p-dioxin
75014 Vinyl chloride
75354 Vinylidene chloride (1,1-Dichloroethylene)
1330207 Xylenes (isomers and mixture)
0 Radionuclides (including radon)[e]
0 Selenium Compounds

TABLE 2.8 (CONTINUED)
1990 CAAA Air Toxics List

CAS Number/Chemical Name	CAS Number/Chemical Name	CAS Number/Chemical Name	CAS Number/Chemical Name	CAS Number/Chemical Name	CAS Number/Chemical Name
133904 Chloramben	106934 Ethylene dibromide (Dibromoethane)	101779 4,4-Methylenedianiline			
57749 Chlordane	107062 Ethylene dichloride (1,2-Dichloroethane)	91203 Naphthalene			
7782505 Chlorine	107211 Ethylene glycol	98953 Nitrobenzene			
79118 Chloroacetic acid	151564 Ethylene imine (Aziridine)	92933 4-Nitrobiphenyl			
532274 2-Chloroacetophenone	75218 Ethylene oxide	100027 4-Nitrophenol			
108907 Chlorobenzene	96457 Ethylene thiourea	79469 2-Nitropropane			
510156 Chlorobenzilate	75343 Ethylidene dichloride (1,1-Dichloroethane)	684935 N-Nitroso-N-methylurea			
67663 Chloroform		62759 N-Nitrosodimethylamine			
107302 Chloromethyl methyl ether		59892 N-Nitrosomorpholine			
126998 Chloroprene					
1319773 Cresols/Cresylic acid (isomers and mixture)					

95487	o-Cresol
108394	m-Cresol
106445	p-Cresol
98828	Cumene
94757	2,4-D, salts and esters
3547044	DDE

Source: 1990 CAAA

Note: For all listings that contain the word “compounds” and for glycol ethers: Unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (i.e., antimony, arsenic, etc.) as part of that chemical’s infrastructure.

[a] X’CN where X = H’ or any other group where a formal dissociation may occur. For example, KCN or $Ca(CN)^2$.

[b] Includes mono- and di-ethers of ethylene glycol, diethylene glycol and triethylene glycol $R\text{-}(OCH^2CH^2)n\text{-}OR'$ where:
n = 1, 2, or 3
R = alkyl or aryl groups
R’ = R, H or groups which, when removed, yield glycol ethers with the structure: R-(OCH2CH)n-OH. Polymers are excluded from the glycol category.

[c] Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral-derived fibers) of average diameter 1 μm or less.

[d] Includes organic compounds with more than one benzene ring and a boiling point greater than or equal to 100°C.

[e] A type of atom that spontaneously undergoes radioactive decay.

and controls located at the POTW….” Non-industrial POTWs are all other POTWs not meeting the industrial POTW definition.

On March 22, 2002, EPA proposed amendments to the POTW NESHAP final rule after reaching an agreement on November 16, 2001, in response to litigation filed by the Pharmaceutical Research and Manufacturers of America (PhRMA). The litigation was driven by PhRMA’s concern that industrial POTWs might be subject to permitting that would otherwise not apply and that such POTWs might elect not to accept wastewater for treatment. The proposed amendments would rescind 40 CFR Part 63.1580(c), which states: “… if an industrial major source complies with applicable NESHAP requirements by using the treatment and controls located at your POTWs, your POTW is considered to be a major source regardless of whether you otherwise meet the applicable criteria.” EPA has also proposed to exempt area source industrial POTWs from the CAAA Title V permitting requirements specified in 40 CFR Part 70 Section 502(a) and to exempt new and existing non-industrial POTWs that are area sources from the notification requirements in the POTW NESHAP. In addition, EPA has determined that the generally available control technology (GACT) requirements for new and existing non-industrial POTW area sources should be no control.

The final rule does not require additional controls for existing industrial and non-industrial major sources. However, as part of the POTW MACT standard, EPA has explicitly stated that industrial POTWs are responsible for complying with applicable NESHAP wastewater control requirements that the industrial discharger may have.

New or reconstructed non-industrial POTWs are required to cover primary treatment units or to demonstrate that the fraction of plant HAP mass loading emitted at the primary treatment units does not exceed 0.014.

New or reconstructed industrial POTWs are required to comply with either the industrial NESHAP discharger requirements or the non-industrial POTW MACT standards, whichever is more stringent.

Reconstruction as defined in 40 CFR 63.1595 means: “… the replacement of components of an affected or a previously unaffected stationary source such that:

- The fixed capital cost of the new components exceeds 50% of the fixed capital cost that would be required to construct a comparable new source; and
- It is technologically and economically feasible for the reconstructed source to meet the relevant standard(s) established by the Administrator (or a State) pursuant to section 112 of the Act. Upon reconstruction, an affected source, or a stationary source that becomes an affected source, is subject to relevant standards for new sources, including compliance dates, irrespective of any change in emissions of HAP from that source.”

Based on information provided by various POTW representatives, EPA has predicted that there will be no new or reconstructed major POTW sources within the next 5 years, i.e., by December 31, 2004. (Preamble to final rule, Section IV. Summary of Impacts, *Federal Register* Vol. 64, No. 206/10/26/99, p. 57575.)

2.4.1 RESIDUAL RISK ANALYSIS

In addition to the implementation of MACT standards to protect human health, EPA under Section 112 (f) of the 1990 CAAA is required to perform residual risk analyses 8 years after control technologies are installed. Residual risk is the estimated increased risk of cancer to the maximum exposed individual (MEI) created by the emissions of HAPs from a source after implementation of MACT.

Human health risk assessments generally consist of four phases or steps: hazard identification, dose–response assessment, exposure assessment and risk characterization. For a description of the risk assessment process, the reader is referred to EPA's *Residual Risk Report to Congress*, Office of Air Quality Planning and Standards, U.S. EPA, Research Triangle Park, NC, April 14, 1998, 191 pp., which is located at www.epa.gov/ttnuatw/risk/rrisk.pdf; www.epa.gov/ttn/oarpg/t3/reports/risk-rep.pdf.

Once completed, results of the residual risk analysis are used to determine whether additional emissions reductions are required. EPA may be required to promulgate additional control requirements for any source category in which one or more sources has a site residual risk greater than one in a million after MACT (CAAA, Section 301, (f) (2) (A)). Decisions to require additional controls will be based on results of the residual risk assessment in conjunction with cost, energy and safety requirements, as well as other relevant factors.

2.4.2 ACCIDENTAL RELEASE AND PREVENTION PROGRAM (RISK MANAGEMENT PLANS)

Another important part of Title III that affects many POTWs is the Accidental Release and Prevention Program, which is closely related to the U.S. Department of Labor Occupational Safety and Health Administration's (OSHA) Process Safety Management (PSM). These regulations will impact POTWs that store hazardous chemicals such as chlorine, sulfur dioxide and ammonia above certain thresholds. Digester gas was originally listed, but was subsequently delisted. The purpose of these regulations is to reduce the number and severity of accidental releases of toxic and flammable substances.

The EPA Clean Air Act Risk Management Plan (RMP) (Reference EPA 550B/99-002, 1999) requirements are outlined in Section 112 (r) of the CAAA and are detailed in 40 CFR Part 68. The OSHA PSM requirements are described in 29 CFR 1910.119. Both the EPA and OSHA regulations require the owner or operator of an affected facility to prepare and implement a management plan to prevent, minimize and respond to accidental releases. While the OSHA PSM and EPA RMP regulations contain many similar requirements, PSM focuses on worker safety and onsite impacts, whereas RMP addresses offsite impacts of chemical releases.

2.4.2.1 Applicability of RMP and PSM

If a facility stores a regulated substance in quantities exceeding a certain threshold, then the RMP and PSM requirements must be met. There are 140 regulated substances under these two programs. The RMP and PSM regulations have a slightly different list of chemicals and thresholds. For wastewater and water treatment plants, the chemicals that are most commonly found and their thresholds are shown in Table 2.9.

Municipalities such as POTWs and water treatment plants are exempt from the OSHA PSM regulations. However, many states have been approved by OSHA to administer the PSM program and have elected not to exempt municipalities. Only in these states will wastewater and water treatment plants be required to comply with the OSHA PSM requirements. The list of states is available from OSHA.

2.4.2.2 Requirements of RMP and PSM

For plants that must comply, submittal of a single RMP to EPA and local agencies was required by June 21, 1999. Portions of the RMP are to be made publicly available by EPA and a public meeting is required. Unlike the RMP, a submittal was not required for compliance with the PSM regulation. The PSM plan for most plants was due in May, 1997.

RMP and PSM programs have several different requirements, many of which are similar or identical. The PSM and RMP regulations are applicable on a process-by-process basis. All processes subject to PSM must comply with identical regulatory requirements. However, processes covered by RMP are subject to one of three different RMP compliance programs, each having progressively stricter standards. The criteria for determining which RMP program a facility must comply with are summarized below:

- Program 1: If a facility has not had an accidental release of a chemical within the past 5 years and can demonstrate that the worst-case accidental release of a chemical will not result in a toxic or explosive impact to a public receptor outside the plant fence line, then the facility is eligible for Program 1. The Program 1 provisions are relatively simple and primarily involve coordinating emergency response procedures with local emergency planning agencies.

TABLE 2.9
Chemicals and Their Thresholds for Applicability for RMP and PSM

Chemical	OSHA PSM Threshold (lbs)	EPA RMP Threshold (lbs)
Chlorine	1500	2500
Sulfur dioxide	1000	5000
Ammonia (anhydrous)	10,000	10,000
Ammonia (aqueous, >20%)	10,000	10,000
Ozone	100	Not Regulated
Hydrogen peroxide	7500	Not Regulated

Source: http://www.epa.gov/swercepp/rules/listrule.html, 40 CFR Parts 9 and 68 [FRL-4828-6], List of Regulated Substances and Thresholds for Accidental Release Prevention; Requirements for Petitions Under Section 112(r) of the Clean Air Act as amended.

- Program 2: If a facility does not qualify for Program 1 or 3 (described below), it falls into Program 2. Program 2 facilities must meet requirements that are a streamlined version of the Program 3 requirements.
- Program 3: Certain designated high-risk industries (not wastewater and water treatment plants) are required to meet the provisions of Program 3. Also, if a facility is subject to the Federal OSHA PSM program, it falls into Program 3. Program 3 contains all of the requirements of PSM and, in addition, includes an offsite consequence analysis.

RMP Programs 2 and 3 requirements are described in the subsections below.

2.4.2.3 Hazard Assessment/Offsite Consequence Analysis

The hazard assessment evaluates the offsite consequences of an accidental release of a regulated substance and must include a determination of the population outside the plant boundaries that would be affected by a release. In addition, receptors such as schools, hospitals and parks located within the affected area must be identified. Air dispersion modeling or EPA look-up tables can be used to determine the distance at which either a toxic concentration or explosive endpoint of a released substance might occur.

2.4.2.4 Prevention Program

A program must be implemented for preventing accidental releases of regulated substances that include the following elements:

- **Process Hazard Analysis (PHA):** An analysis of each regulated process must be conducted to identify and evaluate potential safety hazards. Recommendations must be made to eliminate or reduce the hazards identified to prevent or minimize the chances of an accidental release.
- **Operating Procedures:** Written operating procedures that provide clear instructions for safely conducting activities associated with the regulated process must be prepared.
- **Training:** Personnel operating or maintaining the process must be trained in safe work practices. Refresher training is required at least every 3 years and all training must be thoroughly documented.
- **Mechanical Integrity:** A program must be implemented to ensure that equipment is maintained and installed to minimize the risk of releases and must include a preventive maintenance program, testing procedures and a spare-parts control system.
- **Incident Investigation:** A procedure must be established for investigating the cause of an incident that results in release of a regulated chemical.
- **Process Safety Information:** This includes information regarding chemical hazards, safety equipment and process diagrams.
- **Compliance Audit:** A formal audit is required at least every 3 years to evaluate the effectiveness of the program by identifying deficiencies and assuring corrective actions.

For processes covered by either the RMP Program 3 or OSHA PSM requirements, the following additional elements are required for a prevention program:

- A written procedure to manage changes made to the process
- A procedure for a pre-startup review of the process
- A system to investigate incidents that did occur or could have resulted in a release
- A method to ensure that any contractors working on the process are properly trained
- A program to ensure employee participation in PSM/RMP programs
- A permit program for performing hot work such as welding or cutting in a regulated process area

2.4.2.5 Emergency Response Program

For PSM and RMP Programs 2 and 3, an emergency response program must be developed to provide guidance to employees on what to do in the event of a chemical discharge emergency. Issues that must be addressed include lines of communication, evacuation procedures, coordination with local response agencies such as fire departments, training, drill procedures and use of safety and emergency equipment. For RMP Program 1, facilities only need to coordinate response actions with local emergency response agencies.

2.4.2.6 RMP and PSM Approach

A properly prepared RMP/PSM program will provide a system to safely manage storing and handling hazardous chemicals, effectively communicate the actual potential risks to the public, increase personnel safety awareness and decrease the risk of accidental releases. The following issues need to be considered when preparing an RMP/PSM program.

2.4.2.6.1 Decreasing Material Inventory

If the inventory of a regulated chemical in a process can be reduced to a level below the listed threshold, then the RMP/PSM program will not be required. For example, if a wastewater treatment plant currently stores three 1-ton sulfur dioxide cylinders in a dechlorination process, then it should be determined whether the maximum inventory could be reduced to two cylinders, dropping the level below the threshold of 5,000 pounds and therefore meeting the regulations. Before reducing the chemical inventory, the required chemical dosages, flow rates and chemical delivery times should be considered to ensure sufficient chemicals are available to meet the process requirements. To possibly reduce the inventory of digester gas, it should be determined whether the volume of gas stored can be decreased by reducing the gas storage pressure or eliminating the use of storage vessels.

2.4.2.6.2 Use Refined Modeling to Minimize Distance in Offsite Consequence Analysis

The RMP regulations require that the offsite effects of a worst-case accidental release be presented. The conditions under which a worst-case release is assumed to occur are, for the most part, defined by conservative regulations, resulting in an unrealistic, larger release zone of influence than would most likely occur. To present a more realistic representation of the accidental release consequences, alternative release scenarios are required. Proper presentation of the alternative release scenario is important to help communicate to the public that the probability of the worst-case scenario's occurring is low and that a more realistic scenario would have a less severe effect. The alternative scenario allows more realistic assumptions for parameters such as wind speed, chemical release rate and atmospheric stability, which result in smaller release zones of influence. The method used for calculating the dispersion should be carefully selected since some methods and models available are overly conservative. For example, Figure 2.2 shows the results of air dispersion modeling for the release of a 1-ton chlorine cylinder using conservative EPA look-up tables compared with the simplified area locations of hazardous atmospheres (ALOHA) model and the more refined dense gas dispersion (DEGADIS) computer dispersion model.

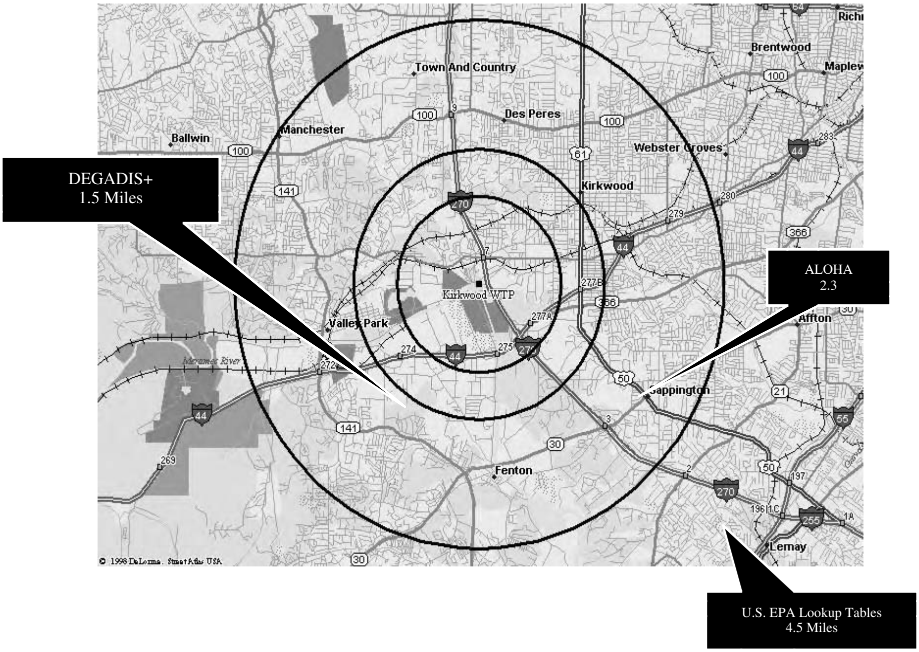


FIGURE 2.2 Release of Cl_2 from a 1-ton chlorine gas cylinder as predicted by Degadis and Aloha Air Dispension Models and EPA look-up tables.

2.4.2.6.3 Select Appropriate Method for the PHA

A thorough PHA will identify potential system hazards and methods to prevent or minimize the causes and consequences of an accidental release. The PHA analysis must be conducted systematically to determine whether process deviations can lead to undesirable consequences. Several methods are available to conduct a PHA; the method selected will depend on the process complexity and RMP program classification. The hazard and operability (HazOp) study is a common PHA methodology that provides a means of systematically reviewing a process to identify potential hazards. The HazOp study typically proceeds sequentially through the pieces of equipment that make up the process. The process is partitioned into nodes that are composed of one or more pieces of equipment where there are distinct process parameters. The regulations require that a person experienced in conducting PHAs lead the analysis.

Additional guidance information regarding RMP can be obtained from EPA's World Wide Web site at http://www.epa.gov/ceppo/acc-pre.html.

2.5 TITLE V: OPERATING PERMITS

Title V of the 1990 CAAA established a federal operating permit program. As part of this program, affected sources are required to submit one consolidated operating permit application that documents all federally applicable permit requirements. The Title V permit program was modeled after the Clean Water Act NPDES program. Hundreds of sources that were previously unregulated must now obtain operating permits. The permit program is implemented by individual states; it is a renewable, 5-year permit that requires extensive information gathering, record keeping, monitoring and reporting. A Title V permit serves as an umbrella that requires compliance with all regulations, including Titles I and III of the 1990 CAAA and state laws and regulations.

2.5.1 APPLICABILITY

Sources must have a Title V permit if they are:

- Major sources of criteria pollutants or HAPs
- Covered by any NSPS, PSD or NESHAP source categories
- Covered under Title IV Acid Deposition Control (acid rain provisions)
- Covered under Title VI Stratospheric Ozone and Global Climate Protection.

The reason that almost all POTWs are required to have the Title V permit is that they are a major source of criteria pollutants. If a source exceeds the emissions shown in Table 2.10, it is required to obtain a Title V permit. Like the PSD major source determination, fugitive emissions are not required to be considered for criteria pollutants regulated under Title I. However, fugitive emissions of HAPs, which are regulated under Title III, are required to be counted in calculating emissions to compare with the HAP threshold for Title V permitting. Fugitive emissions can be obtained by using models, emission factors and direct measurements, as described in Chapters 13 and 14.

TABLE 2.10
Title V Applicability Threshold

Pollutant[a]	Designation	Major Source Trigger (tpy)
VOC/NO_X	Marginal	100
VOC/NO_X	Moderate	100
VOC/NO_X	Serious	50
VOC/NO_X	Severe	25
		25
VOC/NO_X	Extreme	10
CO	Serious	50
PM_{10}	Serious	70
HAPs[b]	NA	10 tpy of any single HAP and 25 tpy of total HAPs

[a] Under CAA Section 182 (f), EPA may exempt certain major NOx sources where NOx reductions would "not contribute to attainment of the national ambient air quality standard in the area" Also, major source threshold applies to VOC or NOx emissions, not combined emissions.

[b] HAPs are covered under Title III of the 1990 CAAA; all the other pollutants listed are covered under Title I.

Applicability determinations and subsequent compliance with Title V requirements can be viewed as a multistep process that includes:

Step 1: Complete a facility-wide emissions inventory for criteria pollutants and regulated HAPs. The emissions inventory must include all point, area and fugitive sources. This is required to determine whether major source status is triggered for either Title I or Title III. Also, calculated emissions will be used to set limitations on emissions. The methods used for estimating emissions must be clearly defined and example calculations must be included.

Step 2: Assess applicable federal or state regulations. All applicable regulations must be identified for each source and each pollutant. These applicable regulations will become part of the permit conditions.

Step 3: Develop methods to demonstrate compliance with permit conditions. These methods could be as simple as monitoring digester gas usage in a flare and using emission factors to calculate emissions. More-complex and -costly methods could include installing a monitor that continuously samples gases in a stack and analyzes the gas for specified pollutants.

Step 4: Develop a system for record keeping and reporting that will demonstrate to the regulatory agency that the source is in compliance with all permit conditions.

Table 2.11 lists POTW sources and the corresponding capacity or rating that would emit pollutants at levels exceeding the major source thresholds, thereby requiring a Title V permit. The emissions from all sources must be added together;

TABLE 2.11
Sources at a POTW That May Require a Title V Permit

Source Type	Total Capacity or Rating Requiring Permit (attainment area)	Total Capacity or Rating Requiring Permit (severe non-attainment area)
Incinerator	60 dry tons per day	15 dry tons per day
Boilers	150 MMBTU/hr	40 MMBTU/hr
Digester Gas Engines	300 hp	75 hp
Liquid Treatment Process	Plant > 30 mgd with high industrial loading	Plant > 30 mgd with high industrial loading

therefore, a combination of sources smaller than those shown in Table 2.11 could cause a POTW to exceed the Title V thresholds. Table 2.11 shows that the thresholds are much lower for severe non-attainment areas, meaning relatively small sources emit pollutants in excess of the thresholds that require a Title V permit. For example, a small 75-hp digester gas engine could cause a POTW to require a Title V permit.

2.5.2 FEDERALLY ENFORCEABLE STATE OPERATING PERMITS (FESOPS) OR SYNTHETIC MINOR

One possible way for a POTW to place itself outside the jurisdiction of a Title V permit is to transform itself from a major source to a minor source. Alternative operating scenarios can be developed, as described below, to reduce the HAPs/NOx emissions from POTWs, thereby enabling them to be operated under a FESOP or synthetic minor. However, FESOP may be revoked if a POTW is expanded to the point of its becoming a major source, thereby placing it under a Title V Permit.

2.5.3 ALTERNATE OPERATING SCENARIOS

The Title V permit application process allows scenarios to be identified in which processes may differ from normal. Emission estimates can be calculated for these scenarios and incorporated into the permit to allow the source to operate under different scenarios. This process is important to allow flexibility in POTW operations.

Some examples of alternative operating scenarios at POTWs include the following:

Changes in Liquid Process Parameters. Variations in process parameters such as influent flow rates, number of unit processes (e.g., aeration basins, clarifiers, etc.) on line; aeration rates and influent temperature can have significant influence on emission rates.

Use of Alternative Fuels in Combustion Sources. For example, use of fuel oil in boilers results in significantly higher SO_2 emissions compared with emissions due to natural gas combustion.

Incinerator Emissions. Emissions of many pollutants, such as particulates from incinerators, can vary depending on several factors. For example, when burning higher moisture content sludge cake or during high loadings, more combustion air is required. This results in increased air velocities through the incinerator, especially when burning on an outer hearth. These high velocities can lead to additional particulates being transported with exhaust gases. NO_X and CO emissions can vary greatly depending on several factors, including the amount of excess air. Incinerators run under optimal operational conditions reduce emissions of the criteria pollutants and other products of incomplete combustion. This leads to overall POTW emissions reduction and lower levels to compare with the triggers.

Future Growth. Increases in wastewater flows or solids loading will likely result in increases in air emissions. Any planned plant expansions should be considered in evaluating conditions that might result in increased emissions. For example, if it is economically feasible and justified, instead of expanding plant capacity, consider constructing new treatment facilities at a location not contiguous to existing facilities; this approach could reduce the potential for both the existing and future facility to be classified as a major source.

It is important that all current and future operating scenarios be identified and associated emissions be determined. If this is not properly conducted, the operational flexibility of the plant could be limited, including restrictions on the amount of wastewater and solids that can be processed.

Within 1 year of becoming subject to a Title V permit program, affected sources are required to submit a compliance plan and a permit application. The compliance plan must document how all applicable requirements will be met and also establish a schedule detailing required report submission dates.

Permits are issued for a period of up to 5 years, but are subject to annual certification by the permittee that the facility continues to be in compliance. Change or modifications to the facility may require permit revisions. In addition, changes in applicable federal regulations or standards after permit issuance may require permit modification.

2.6 NATIONAL AIR TOXICS PROGRAM: THE INTEGRATED URBAN STRATEGY

On July 19, 1999, the EPA published a notice in the Federal Register on the Integrated Urban Strategy to reduce public health risks due to air toxics from stationary and mobile sources in the urban areas of the United States. The 1990 CAAA does not provide a definition of “urban.” Urban areas that include a metropolitan statistical area with a population greater than 250,000 people are singled out for air monitoring. However, the possibility of monitoring other urban areas is also mentioned. The U.S. Census Bureau definition does not necessarily apply for regulatory or implementation purposes.

The key components of the strategy are:

- Regulations to address area sources of air toxics at both the national and local level

- Initiatives to address specific pollutants (e.g., mercury) and identify community health risks
- Assessment of air toxics by expanded monitoring and modeling efforts to identify areas of concern, to prioritize efforts for risk reduction and to track the progress of the programs initiated
- Education and outreach activities to inform the public about the strategy and get input for designing and appropriate programs

The goals of the strategy are threefold:

- To reduce the risk of cancer associated with air toxics from all stationary sources by 75%
- To substantially reduce non-cancer risk from area sources (e.g., birth defects and reproductive effects)
- To address environmental justice issues such as disproportionate impacts of air toxic hazards across urban area hot spots and minority and low income areas

The integrated urban air toxics strategy under Sections 112(c)(3) and 112(k) of the 1990 CAAA identified 33 HAPs (see Table 2.12) as having the greatest potential to affect human health in major urban areas. Thirty of these HAPs are associated with 29 area source categories (see Table 2.13), which include POTWs and now sewage sludge incinerators. Sewage sludge incineration has been delisted from the Title III MACT Source Category. Since that time, the U.S.EPA has placed these sources in this program. Area sources are defined as small stationary sources that emit less than 10 tons per year of any single HAP among the 188 HAPs listed in Title III, or 25 tons per year of a combination of HAPs. In 2002, EPA had regulations under development or completed for 16 of these categories. However, as indicated in Section 2.4, in its rule published in the *Federal Register* on March 22, 2002, EPA proposed to exempt area source industrial POTWs from the CAAA Title V permitting requirements specified in 40 CFR Part 70 Section 502(a) and to exempt new and existing non-industrial POTWs that are area sources from the POTW NESHAP notification requirements. EPA also determined that the GACT requirements for new and existing non-industrial POTW area sources should be no control.

2.7 OTHER REGULATIONS

Many states and local agencies have established air quality regulations that are more stringent than the Federal Clean Air Act. California, Washington, New Jersey and Wisconsin have established regulations regarding the control of HAPs and toxic air pollutants. These rules often regulate emissions of more toxics than the 188 HAPs regulated under Title III. For example, California's and Wisconsin's toxic air pollutant rules regulate more than 400 compounds. Also, many states require operating and construction permits for sources that are much smaller than those that require permits under the 1990 CAAA. In addition, several states and agencies have established rules that regulate the control of odorous emissions.

TABLE 2.12
List of Urban HAPs for the Integrated Urban Toxics Strategy

HAP	CAS No. +HAP
Acetaldehyde	75070
Acrolein	107028
Acrylonitrile	107131
Arsenic compounds	
Benzene	71432
Beryllium compounds	
1,3-Butadiene	106990
Cadmium compounds	
Carbon tetrachloride	56235
Chloroform	67663
Chromium compounds	
Coke oven emissions	8007452
1,2-dibromoethane	106934
1,2-dichloropropane (propylene dichloride)	78875
1,3-dichloropropene	542756
Ethylene dichloride (1,2-dichloroethane)	107062
Ethylene oxide	75218
Formaldehyde	50000
Hexachlorobenzene	118741
Hydrazine	302012
Lead compounds	
Manganese compounds	
Mercury compounds	
Methylene chloride (dichloromethane)	75092
Nickel compounds	
Polychlorinated biphenyls (PCBs)	1336363
Polycyclic organic matter (POM)	
Quinoline	91225
2,3,7,8-Tetrachlorodibenzo-p-dioxin (and congeners and TCDF congeners)	1746016
1,1,2,2-Tetrachloroethane	79345
Tetrachloroethylene (perchloroethylene)	127184
Trichloroethylene	79016
Vinyl chloride	75014

Source: http://www.epa.gov/ttn/oarpg/t3/fact_sheets/urbanfs2.pdf

State and local regulations should always be carefully evaluated to determine whether they are more stringent than federal regulations.

2.8 SUMMARY

Air quality compliance requirements at POTWs have become increasingly stringent and complex over the years. A particular regulatory focus has been VOCs. In addition

TABLE 2.13
Area Source Categories That Are Already Subject to Standards, Will Be Subject to Standards and Are Being Listed

Categories Already Subject to Standards

Chromic acid anodizing
Industrial boilers

Categories That Will Be Subject to Standards

Commercial sterilization facilities
Other solid waste incinerators (human/animal cremation)
Decorative chromium electroplating
Dry cleaning facilities
Halogenated solvent cleaners
Hard chromium electroplating
Hazardous waste combustors
Institutional/commercial boilers
Medical waste incinerators
Municipal waste combustors
Open burning scrap tires
Portland cement
Secondary lead smelting
Stationary internal combustion engines

Categories Being Listed

Cyclic crude and intermediate production
Flexible polyurethane foam fabrication operations
Hospital sterilizers
Industrial inorganic chemical manufacturing
Industrial organic chemical manufacturing
Mercury cell chlor-alkali plants
Gasoline distribution StageI
Municipal landfills
Oil and natural gas production
Paint stripping questions
Plastic materials and resins manufacturing
Publicly owned treatment works
Synthetic rubber manufacturing

Source:
http://www.epa.gov/ttn/oarpg/t3/fact_sheets/urbanfs2.pdf

to a series of CAAAs at the federal level, many POTWs are faced with meeting state or local requirements that are even more stringent than the federal regulations. It is prudent for POTWs to keep abreast of continuing activities in the regulatory arena and to understand the impact of these activities on their own operations.

3 Occurrence of Volatile Organic Compounds in Wastewater

Prakasam Tata, Tom Card and Cecil Lue-Hing

CONTENTS

3.1 Introduction 37
3.2 Sources of Volatile Organic Compounds in Wastewater 38
  3.2.1 Water Supply 38
  3.2.2 Industries 39
  3.2.3 Commercial Establishments 39
  3.2.4 Household and Consumer Products 39
  3.2.5 Surface Runoff 39
  3.2.6 Chemical and Biogenic Reactions Occurring during Treatment 41
3.3 Concentrations of VOCS in Wastewater 42
  3.3.1 VOC Concentrations in Domestic vs. Industrial Sewerage Systems 42
  3.3.2 VOC Concentration of POTW Influents 42
  3.3.3 EPA 40-City Study 45
  3.3.4 RTI Study 46
  3.3.5 Ontario, Canada Study 47
  3.3.6 East Bay Municipal Utility District (EBMUD) 47
  3.3.7 Association of Metropolitan Sewerage Agencies (AMSA) 47
  3.3.8 New York City Study 49
3.4 Summary 56
References 56

3.1 INTRODUCTION

A key priority for POTWs in devising an approximate air quality compliance strategy is to gain a good understanding of the sources of VOCs in wastewater and the concentrations in which the VOCs are present. This chapter provides an overview

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

of sources of VOCs in wastewater and describes various efforts by municipal and regulatory agencies to quantify VOC loads to POTWs.

3.2 SOURCES OF VOLATILE ORGANIC COMPOUNDS IN WASTEWATER

Sources contributing to the occurrence of VOCs in wastewater can be broadly characterized as:

- Water supply
- Industries
- Commercial establishments
- Household and consumer products
- Surface runoff
- Chemical and biogenic reactions that occur during water and wastewater treatment.

3.2.1 WATER SUPPLY

Chloroform is formed during the chlorination of municipal water supplies and wastewater effluents; methylene chloride and carbon tetrachloride may also be formed. When bromination is used to disinfect water supplies and wastewater effluents, bromoform may be formed.

3.2.2 INDUSTRIES

Many VOCs are used in various industrial manufacturing and process applications. Industrial discharges containing spent or trace VOCs are a source of VOCs. Based on operational conditions of treatment process units and properties of the VOCs, some or all of these trace amounts may volatilize. Industrial categories such as metal finishing, synthetic organic chemical manufacturing, textiles, petrochemicals, petroleum refining, plastics, semiconductors, glass manufacturing, pharmaceuticals, dyes, synthetic rubber, paint and pigment, electroplating, pesticides, degreasing operations, explosives and natural and synthetic resins use a variety of VOCs.

In a report published in 1989, EPA estimated VOC losses from 1671 POTWs.[1] These POTWs accounted for 81% of the total wastewater flows and received 97% of the indirect discharges from industries. Estimates indicated that greater than 98% of the VOCs were discharged by 11 industrial categories for the following seven potential hazardous air pollutants:

1. Carbon tetrachloride
2. Trichloroethylene
3. Perchloroethylene
4. Methylene chloride
5. Ethylene dichloride
6. Chloroform
7. Acrylonitrile.

The chemicals contributed most by industries are benzene, methylene chloride, trichloroethylene and carbon tetrachloride.[2] Benzene is found in petroleum-refinery and oil-production industrial wastewater. It is used by several industries that produce consumer products such as fabric adhesives, antiperspirants, deodorants, detergents, oven cleaners, paintbrush cleaners, dandruff remover and shampoo, tar remover, solvents and thinners and can enter the sewer system through wastewater discharged from these industries. Carbon tetrachloride, trichloroethylene and ethylene dichloride are used as industrial solvents and can be found in wastewaters discharged from degreasing, dewaxing and other types of industrial cleaning operations. Methylene chloride is used as a paint-stripping agent in industries and as a solvent in other applications; it is also used in consumer product industries manufacturing leather coatings, oven cleaners, tar removers, wax, degreasers and spray deodorants. Perchloroethylene is used to manufacture household products such as contact cements, detergents, paintbrush cleaners, perfumes, degreasers, etc., and can be found in wastewaters from these industries. Chloroform is formed during water and wastewater disinfection and is also used to manufacture household products such as liniments, degreasers and cough medicine.

3.2.3 COMMERCIAL ESTABLISHMENTS

Commercial laundries, hospitals, jails and other similar establishments that use dry-cleaning fluids, solvents and products containing VOCs and discharge wastewater into sewers also contribute VOCs to POTWs.

3.2.4 HOUSEHOLD AND CONSUMER PRODUCTS

Wastewater discharged from households can contain many VOCs. These include various household products, such as cleaning compounds, disinfectants, solvents, personal hygiene compounds, automotive supplies, mothballs, lawn and garden products, laundry products, waste paint, photographic chemicals, medicines, etc. These materials may contain benzene, bis-2-ethyl hexyl chloride, chloroform, 1,1, dichloroethane, 1,2 dichloro ethylene, di-n-butylphthalate, methylene chloride, pentachlorophenol, tetrachloro ethylene, toluene, 1,1,1-trichloroethane, trichloroethylene and phenol. The chlorine bleach used in washing machines can also form chloroform.

3.2.5 SURFACE RUNOFF

Runoff from combined sewer area overflows, particularly in heavily urbanized areas, was reported to contain a higher concentration of VOCs than areas having separate sewers.[3] The influent concentrations of benzene, toluene, xylenes, cyclohexanes and alkanes reported for the treatment facilities in the metropolitan Chicago area are shown in Table 3.1. In general, the relative distribution of benzene, toluene, xylenes, cyclohexanes and alkanes are similar at the West-Southwest Sewage Treatment Works (STW) (currently known as the Stickney Water Reclamation Plant), North Side and Calumet Sewage Treatment Works. Although the exact reason for the elevated concentrations of these compounds in the wastewater of these treatment facilities is not known, it is possible that gasoline spilled on streets, parking lots and

TABLE 3.1
Concentrations of Principal Non-Listed VOCs

	VOC Concentration (μG/M^3)					Facility Operational Characteristics			
Treatment Facility	Benzene	Toluenes	Xylenes	Cyclohexanes	Alkanes	Influent Flow (mgd)	Combined Sewer Area* (mi2)	Service Area* (mi2)	Combined Sewer Area (%)
West-Southwest	12.75	35.57	35.34	8.77	2.58	638.3	176.1	259.8	67.8
North Side	7.35	26.15	13.76	4.29	1.57	290.3	96.5	142.4	67.8
Calumet	15.59	42.95	18.42	0.97	0.57	270.9	88.0	299.4	29.4
O'Hare	0.30	12.50	ND	ND	ND	64.9	13.8	65.2	21.2
John E. Egan	0.20	3.30	ND	ND	ND	22.4	0.0	44.6	0.0
Hanover Park	0.30	11.30	ND	ND	ND	11.8	0.0	11.2	0.0
Lemont	0.30	1.50	ND	ND	ND	1.2	0.0	20.9	0.0

Source: Noll, K.E. and De Paul, F.T., *Emissions of Volatile Organic Compounds from the Sewage Treatment Facilities of the Metropolitan Sanitary District of Greater Chicago*, Report to the Metropolitan Sanitary District of Greater Chicago, 1987.

ND = non-detectable

* From Facilities Planning Study — MSDGC Update Supplement and Summary, May 1984

Benzene derivatives: isopropylbenzene, n-propylbenzene, (1-methylpropyl)benzene, dichlorobenzene isomers

Toluene derivatives: 2, 3, or 4 ethyltoluene, 4,4-isopropyltoluene

Xylenes: m-xylene, o-p-xylene

Cyclohexanes: methylcyclohexane, ethylcyclohexane, dimethylcyclohexane isomers, trimethylcyclohexane, ethylmethylcyclohexane isomers, isopropylcyclohexane, tetramethylcyclohexane

Alkanes: hexane, octane, nonane

gasoline service stations contribute to the surface runoff, which finds its way to the treatment facilities. The three treatment facilities have the three largest combined sewer overflow areas, namely, 172, 96 and 88 square miles, respectively, and are, therefore, the primary recipients of discharges from these sources. To determine whether the quantity of gasoline components in the influent of each treatment facility is proportional to the area of combined sewers, Noll and De Paul divided the input loading of the benzene, toluene and xylenes (BTXs), cyclohexanes and alkanes of the three treatment facilities by their respective combined sewerage area associated with each of these treatment facilities; the results are presented in Table 3.2. In general, the measured gasoline component VOC inputs to these treatment facilities are proportional to the combined sewer areas, suggesting that the possible source of these VOCs is from nonpoint runoff to combined sewers.

3.2.6 CHEMICAL AND BIOGENIC REACTIONS OCCURRING DURING TREATMENT

As indicated previously, chlorination byproducts such as chloroform, methylene chloride and carbon tetrachloride can be formed during disinfection of water and wastewater. Bishop et al.[4] reported a University of California, Davis study that investigated chlorination of partially nitrified and nitrified secondary effluent, indicated that 120 micrograms (μg) of trihalomethanes per liter were formed with the nitrified wastewater in comparison to 3 μg of trihalomethanes per liter formed with the partially nitrified wastewater. These compounds are also formed in scrubbers when hypochlorite is used as the scrubber solution.[5,6] Concentrations of benzene, BTX and ethyl benzene in digester gas were reported to be high and were suggested to be due to their removal in sludge streams followed by desorption, formation, or both during the anaerobic digestion process. These concentrations can also be formed by the transformation of toluene and xylenes contained in digester gas during the incomplete combustion of digester gas. Higher concentrations of benzene are formed at lower flame temperatures than at higher temperatures.[7] Biogenic formation of VOCs was also reported during the composting of solid wastes.[8]

TABLE 3.2
Non-Dimensional Concentrations of Principal Non-Listed VOCs in the Influent Sewage

Treatment Facilities	Benzenes	Toluenes	Xylenes	Cyclohexanes	Alkanes
West-Northwest STW	1	2.79	2.77	0.69	0.20
North Side STW	1	3.56	1.87	0.58	0.21
Calumet STW	1	2.75	1.18	0.06	0.04

Source: Noll, K.E. and De Paul, F.T., *Emissions of Volatile Organic Compounds from the Sewage Treatment Facilities of the Metropolitan Sanitary District of Greater Chicago*, Report to the Metropolitan Sanitary District of Greater Chicago, 1987.

3.3 CONCENTRATIONS OF VOCS IN WASTEWATER

In view of the expected publication of the 1990 CAAA, there was a great interest in the POTW community to understand the potential impact on their operations due to VOC emissions contained in the wastewater. Hence, efforts by municipal and regulatory agencies to quantify the VOC loads to POTWs began in the early 1980s. Particularly, major municipalities with a significant industrial waste contribution were very concerned because of a greater potential for VOC emissions from their POTWs than from smaller POTWs. Several studies reported on the occurrence of VOCs and their concentrations in POTW wastewater influent.[3,7,9,10–14]

3.3.1 VOC Concentrations in Domestic vs. Industrial Sewerage Systems

It may be difficult to find a city POTW that treats domestic sewage exclusively. However, in a study for the determination of VOCs conducted on 51 POTWs in California, seven POTWs were identified as typically receiving domestic wastewater with very insignificant amounts of industrial wastewater, the study concluded that the concentration of the total VOCs detected was less than 10 μg/L.[15] Other investigators made similar observations.[14,16]

Levins[16] classified sewers receiving wastewater as residential, commercial and industrial according to the total VOC content of the wastewater transported. Residential sewers typically averaged less than 10 μg VOCs/L. Commercial sewers usually have an average total VOC concentration of less than 25 μg/L; the maximum average observed was 21.4 μg/L. The total VOC concentration of the industrial sewers ranged between 1 to 100 μg/L. Concentrations of the most frequently occurring VOCs, namely ethyl benzene, tetrachloroethene toluene, 1,1,1-trichloroethane and trichloroethene were all above 50 μg/L.

These studies were conducted many years ago, therefore it should not be surprising if the current VOC concentration of influents at these POTWs are considerably lower than in the 1980s because of the significant positive effect of their pretreatment programs on reducing VOC loadings.

3.3.2 VOC Concentration of POTW Influents

The results of a few major studies previously reported are presented herein to illustrate the nonuniformity of both the occurrence and concentrations of VOCs in POTW influent wastewaters. It should be noted that the collection and analysis of wastewater samples for VOCs is difficult and expensive. Most municipal agencies do not have the resources to have an accurate estimate of the daily VOC loadings of their POTWs. Therefore, the influent VOC concentrations presented represent only a snapshot of the values and may vary considerably depending on the time the wastewater samples were collected for analysis.

A report published under a grant from the Water Pollution Control Research Foundation[17] summarized the maximum concentrations of VOCs occurring in the influent of 40 different wastewater treatment plants studied by EPA[18] along with the influent VOC concentrations reported from other studies conducted by the Research

Triangle Institute, North Carolina; East Bay Municipal Utility District, California; Ontario, Canada (Four Plant Study); and EPA Region 4.

The results reported in the above studies are summarized in Table 3.3, which presents the toxicants tested, the percent samples that showed the occurrence of the compounds tested and their maximum concentration.

TABLE 3.3
Frequency of Occurrence and Concentration of Toxicants Found in POTW Influents

Toxicants	Percent Samples Toxicants Found	Maximum Concentration (μg/L)
Acenaphthene	3.1	21
Acenaphthalene	0.3	5
Acrolein	0.0	—
Acrylonitrile	0.3	82
Aldrin	1.4	5
α-BHC	7.6	4.4
α-endosulfan	1.0	2.7
Anthracene	18.1	93
Benzene	60.8	1.56
Benzidine	0.0	—
Benzo (a) anthracene	3.1	15
Benzo (a) pyrene	1.1	10
Benzo (ghi) perylene	0.7	35
Benzo (k) fluoranthene	0.7	5
Benzoflouranthene (3,4)	0.7	5
Bis (2-chloroethoxy) methane	0.7	5
Bis (2-chloroethyl) ether	0.0	—
Bis (2-chloroisopropyl) ether	0.0	—
Bis (2-ethyl hexyl) phthalate	92.3	670
Bis (chloromethyl) ether	0.0	—
Bromoform	2.4	81
Bromophenyl phenyl ether (4)	0.3	5
Butyl benzyl phthalate	57.5	560
Carbon tetrachloride	8.7	1900
Chlordane	0.0	—
Chlorobenzene	12.5	1500
Chlorodibromomethane	2.8	3
Chloroethane	1.0	38
2-Chloroethyl vinyl ether	0.3	10
Chloroform	91.3	430
2-Chloronaphthalene	0.7	7
2-Chlorophenol	3.1	5
4-Chlorophenyl phenyl ether	0.0	—
Chrysene	3.1	15
4,4’-DDD	0.7	0.77
4,4’-DDE	0.0	—

TABLE 3.3 (CONTINUED)
Frequency of Occurrence and Concentration of Toxicants Found in POTW Influents

Toxicants	Percent Samples Toxicants Found	Maximum Concentration (μg/L)
4,4’-DDT	0.3	0.1
dibenzo (a,h) anthracene	0.7	5
1,2-dichlorobenzene	23.3	440
1,3-dichlorobenzene	6.6	270
1,4-dichlorobenzene	17.1	200
3,3’-dichlorobenzidene	0.0	—
dichlorobromomethane	8.3	22
dichlorodifluoromethane	2.4	1000
1,1-dichloroethane	30.9	24
1,2-dichloroethane	14.6	76000
1,1-dichloroethylene	25.7	243
2,4-dichlorophenol	6.9	25
1,2-dichloropane	7.3	2600
1,2-dichloropropylene	2.4	100
dieldrin	0.7	40
diethylphthalate	52.6	42
dimethylphthalate	11.5	110
2,4-dimethylphenol	9.7	55
2,4-dinitrophenol	0.3	7
2,4-dinitrotoluene	1.0	8
2,6-dinitrotoluene	0.3	5
4,6-dinitro-o-cresol	0.0	—
1,2-diphenylhydrazine	1.4	50
di-n-butylphthalate	64.5	140
di-n-octylphthalate	7.0	210
endosulfan sulfate	0.0	—
endrin	0.0	—
endrin aldehyde	0.0	—
ethylbenzene	80.2	730
fluoranthene	7.0	5
fluorene	3.8	5
γ-BHC-Δ	26.0	3.9
heptachlor	5.2	0.5
heptachlor ethoxide	0.7	0.5
hexcholorobenzene	1.4	20
hexachlorobutadiene	0.3	5
hexchlorocyclopentadiene	0.0	—
hexchloroethane	0.7	12
isophorone	1.7	23
Methyl bromide	3.5	164
Methyl chloride	0.0	—
Methylene chloride	92.4	49000

TABLE 3.3 (CONTINUED)
Frequency of Occurrence and Concentration of Toxicants Found in POTW Influents

Toxicants	Percent Samples Toxicants Found	Maximum Concentration (μg/L)
Naphthalene	49.5	150
Nitrobenzene	0.0	—
2-nitrophenol	0.3	—
4-nitrophenol	0.0	—
n-nitrosodimethylamine	0.0	—
n-nitrosodiphenylamine	1.7	—
n-nitrosodi-n-propylamine	0.0	—
PCB-1016, PCB-1221, PCB1232	0.0	—
PCB-1242	4.5	49.6
PCB-1248	0.0	—
PCB-1254	1.0	5.5
PCB-1260	0.0	—
Pentachlorophenol	29.3	640
Phenanthrene	19.9	93
Phenol	79.2	1400
Pyrene	6.6	84
p-chloro-m-cresol	3.1	41
Lindane-γ	3.1	1.4
TCDD (2,3,7,8)	0.0	—
1,1,2,2-tetrachloroethane	6.6	2200
Tetrachloroethylene	94.8	5700
Toluene	95.8	13000
Toxaphene	0.0	—
1,2-trans-dichloroethylene	62.2	200
1,2,4-trichlorobenzene	9.8	4300
1,1,1-trichloroethane	84.7	30000
1,1,2-trichloroethane	7.3	135
Trichloroethylene	90.3	1800
Trichlorofluoromethane	8.7	190
2,4,6-trichlorophenol	4.5	11
Vinyl chloride	5.9	3900

Source: Baillod, C.R., Crittenden, J.C., Mihelcic, J.R., Rogers, T. and Grady, L., Jr., *Critical Evaluation of the State of Technologies For Predicting the Transport and Fate of Toxic Compounds in Wastewater Facilities*, WPCF Research Foundation Project 90-1, December 1990.

3.3.3 EPA 40-CITY STUDY

The EPA 40-City Study examined approximately 280 samples for each toxicant (semivolatile and volatile organics), whereas the other studies covered fewer than five treatment plants and fewer than 20 samples. It should be noted that current toxicant loadings at these treatment plants may be lower now, because implementation of stringent pretreatment requirements and better housekeeping at industrial sites has probably reduced influent toxicant concentrations.

Table 3.4 presents frequently occurring VOCs with the percentage of samples showing their occurrence in the EPA's 40-City Study.

3.3.4 RTI STUDY

In the RTI study, Pellizzari and Little[19] analyzed wastewater samples from a 6.3-million-gallon-per-day (mgd) treatment plant receiving wastewater with an industrial component of about 40% for 33 VOCs. Twelve VOCs, namely acrolein; benzene; chloroform; cumene; 1,2-dichlorobenzene; 1,3-dichlorobenzene; 1,2-dichloroethane; ethyl benzene; toluene; 1,1,1-trichloroethane; trichloro-ethylene; chloromethane and 1,1,2,2-tetrachloroethylene compounds were found within a concentration range of 0.8 to 26.2 μg/L. Acrylonitrile; bis (2-chloroethyl) ether; carbon tetrachloride; chlorobenzene; chloroethane; 2, chloroethyl vinylether; dichlorodifluoromethane; 1,1-dichloroethane; 1,1-dichloroethylene; 1,2-dichloropropane; methylenechloride, 1,1,2,2-tetrachloroethane; 1,1,2-trichloroethane; trichlorofluoromethane; vinyl chloride; bromodichloro-methane; bromomethane; dibromochloromethane; cis-1,3-dichloropropene; trans-1,2-dichloroethylene and trans-1,2-dichloropropene were reported at 0 μg/L.

TABLE 3.4
Most Frequently Occurring VOCs in POTW Influents of the 40 City Study (1982)

VOC	Percent of Samples Present
Toluene	95.8
Tetrachloroethylene	94.8
Methylene chloride	92.4
Bis (2-ethyl hexyl) phthalate	92.3
Chloroform	91.3
Trichloroethylene	90.3
1,1,1-trichloroethane	84.7
Ethyl benzene	80.2
Phenol	79.2
Di-n-butyl phthalate	64.5
Trans-1,2-dichloroethene	62.2
Benzene	60.8
Butyl benzyl phthalate	57.5
Diethyl phthalate	52.6

Source: U.S. EPA, *Fate Of Priority Pollutants In Publicly Owned Treatment Works*, Report 440/1-82-003, 1982.

3.3.5 ONTARIO, CANADA STUDY

Influents of four POTWs were analyzed in this study with methods having a detection limit of less than 1 µg/L. Benzene; chlorobenzene; chloroform; cumene; 1,2-dichlorobenzene; 1,3-dichlorobenzene; 1,4-dichlorobenzene; 1,1-dichloroethane; 1,2-dichloroethane; 1,2-dichloropropane; ethylbenzene; methylene chloride; styrene; tetrachloroethylene; toluene; 1,1,1-trichloroethane; trichloroethylene; xylenes; bromodichloroethane; dibromochloromethane; dibromomethane, cis-1,2-dichloroethene; 1,3-diethyl benzene; 1,4-diethylbenzene; 2 and 3 and 4 -ethyl toluenes; propylbenzene; 1,2,3-trimethyl benzene; 1,2,4-trimethyl benzene and 1,3,5-trimethyl benzene were detected within a concentration range of 0.1 and 1,010 µg/L; the lowest and highest concentrations were for 1,3-dichlorobenzene, chlorobenzene and trichloroethylene, respectively.[20]

3.3.6 EAST BAY MUNICIPAL UTILITY DISTRICT (EBMUD)

The results of the EBMUD study presented by Hellier[21] indicated that the following VOCs were detected in the influent wastewater: benzene; chlorobenzene; chloroethane; chloroform; cumene; 1,2, 1,3 and 1,4 dichloroenzenes; 1,1 and 1,2, dichloroethanes; 1,1, dichloroethylene; ethyl benzene; methyl chloride; methyl ethyl ketone; naphthalene; styrene; tetrachloroethylene; toluene; 1,1,1, trichloroethane; trichloroethylene; acetone; bromodichloromethane; chloromethane; 1,2, dibromomethane; cis-1,2, dichloroethane; trans-1,2, dichloroethylene; freon 113; methyl isobutyl ketone and 1,2,3 trichlorobenzene. The concentrations of these compounds were within the range of 1 to 920 µg/L; 1,2,3, trichlorobenzene; freon 113; trans- 1,2, dichloroethylene; 1,1, dichloroethylene and 1,1, dichloroethane had the lowest concentration of 1µg/L, while tetrachloroethylene had the highest concentration of 920 µg/L.

3.3.7 ASSOCIATION OF METROPOLITAN SEWERAGE AGENCIES (AMSA)

Most of the above studies were conducted more than a decade ago. However, in 1993, AMSA conducted a comprehensive survey by the voluntary participation of its major member agencies when it was negotiating with EPA for developing the MACT rule for POTWs. AMSA collected the results of influent monitoring from 181 POTWs. The objective of this survey was to determine which VOCs are the most important in terms of the occurrence and magnitude of emissions from POTWs. EPA used the data collected by AMSA to develop and publish the final MACT rule for POTWs in 1999.

In Table 3.5, the data obtained in the AMSA survey of 1993 can be compared with the 1985 domestic sewage survey data obtained by EPA. Both of these data sets contain many, if not all of the VOCs listed in Title III of the 1990 CAAA. The average cumulative concentration of the VOCs measured in the AMSA survey is about 10% of the total VOC concentration obtained in the 1985 domestic sewage survey. This reduction in the VOC load of the POTW influents is attributable to the diligent efforts of municipal agencies to enforce pretreatment programs for the purpose of reducing toxic loads to POTWs.

TABLE 3.5
AMSA Recommended Air Toxic Compound List for POTWs

CAS	Chemical Name	U. S. EPA[a] Conc. (μg/L)	AMSA Conc.
1330207	Xylenes (isomers and mixture)		20.99
75092	Methylene chloride (Dichloromethane)	109.00	10.92
108101	Methyl isobutyl ketone (Hexone)		111.42
127184	Tetrachloroethylene (Perchloroethylene)	25.70	8.46
108883	Toluene	203.00	14.97
71556	Methyl chloroform (1,1,1-Trichloroethane)	54.70	4.63
67663	Chloroform	66.60	5.90
107028	Acrolein	0.01	41.86
71432	Benzene (including benzene from gasoline)	124.00	3.09
106467	1,4 Dichlorobenzene (p)	7.75	6.97
100414	Ethyl benzene	128.00	2.55
79016	Trichloroethylene	23.90	1.44
100425	Styrene		1.19
78933	Methyl ethyl ketone (2-Butanone)		12.26
108907	Chlorobenzene	0.04	3.38
75354	Vinylidene chloride (1,1-Dichloroethylene)	0.27	0.80
91203	Naphthalene	45.00	1.79
107062	Ethylene dichloride (1,2 Dichloroethane)	2.37	0.59
107131	Acrylonitrile		3.18
56235	Carbon tetrachloride	5.21	0.06
75014	Vinyl chloride	2.10	0.02
117817	Bis(2 ethylhexyl)phthalate (DEHP)	44.90	NA
542881	Bis(chloromethyl)ether	0.02	NA
75252	Bromoform	0.00	NA
67561	Methanol		NA
84742	Dibutylphthalate	0.85	NA
111444	Dichloroethyl ether (Bis(2-chloroethyl)ether)	0.02	NA
131113	Dimethyl phthalate	0.05	NA
123911	1,4 Dioxane (1,4-Diethyleneoxide)		ND
106934	Ethylene dibromide (1,2-Dibromoethane)		ND
67721	Hexachloroethane	0.00	NA
74839	Methyl bromide (Bromomethane)	0.02	NA
74873	Methyl chloride (Chloromethane)	0.71	NA
98953	Nitrobenzene	0.11	NA
87885	Pentachlorophenol	4.49	NA
108952	Phenol	1440.00	NA
1336363	Polychlorinated biphenyls (Aroclors)	0.02	NA
78875	Propylene dichloride (1,2-Dichloropropane)	0.00	NA
79345	1,1,2,2-Tetrachloroethane	0.02	NA
120821	1,2,4-Trichlorobenzene	0.02	NA
79005	1,1,2-Trichloroethane	7.16	NA
88062	2,4,6-Trichlorophenol	0.89	NA

Source: Association of Metropolitan Sewerage Agencies, 1993 Unpublished data.

[a] Office of Air Quality and Performance Standards ,U.S.EPA; NA: No Analysis; ND: Not Detected

3.3.8 New York City Study

The New York City Department of Environmental Protection (NYCDEP) recently completed a comprehensive study and published a report[22] showing the VOC emission rates from its 14 water pollution control plants (WPCPs) and associated health risks to the communities residing in the vicinity of these plants. The ranges of concentrations of the various VOCs detected in the raw sewage, primary influent, primary effluent, returned activated sludge, aeration tank and final effluent of NYCDEP's 14 WPCPs during summer and winter are presented in Tables 3.6 and 3.7. Tetrachloroethene showed the highest concentrations in both summer and winter at 60 and 58 μg/L, respectively. Surprisingly, acetone showed the highest concentration of 570 μg/L in the final effluent, compared with an influent concentration of 250 in winter; however, acetone is not classified as a Title III VOC.

In this study, influent VOC data from three WPCPs (North River, Rockaway and Wards Island) were collected in detail to statistically analyze significant differences between the VOC concentrations of samples collected in summer and winter, samples collected during a.m. and p.m. and samples collected during weekday and weekend. Samples were collected at seven locations: raw influent, primary influent, primary effluent, returned activated sludge, aeration pass-B, aeration pass-C and effluent. The results of the statistical analyses are shown in Tables 3.8, 3.9 and 3.10. The following VOCs showed significant variation in their concentration between the two seasons at numerous locations, but the differences are not consistently either high or low with respect to the seasons:

- At the North River WPCP, chloroform (five of seven locations), benzene (seven of seven locations), 4-methyl-2-pentanone (three of five locations) and toluene (six of seven locations)
- At the Rockaway WPCP, cis-1,2-dichloroethene (three of six locations) and chloroform (four of seven locations)
- At the Wards Island WPCP, chloroform (three of five locations) and m- and p-xylenes (two of three locations)

The differences in VOC concentrations between the weekdays and weekend are not statistically significant with the exceptions of 1,1,1-trichloroethane (five of seven locations) and tetrachloroethene (four of six locations at the North River WPCP). In particular, the influent wastewater VOC concentrations did not show statistically significant variation in weekday/weekend, with the exception of 1,1,1-trichlorethane; chloroform and tetrachloroethene at the North River WPCP and trichloroethene and total xylenes at the Rockaway WPCP.

Statistical analysis of the data collected for studying diurnal variation did not show a statistically significant variation in a.m./p.m. VOC concentrations with the exception of trichloroethene (six of six locations) and toluene (six of six locations) at the Wards Island WPCP.

The variability in the occurrence of various VOCs and their concentrations at various treatment plants and significant differences in their concentrations between seasons make it difficult to accurately predict the VOC loadings to treatment plants

TABLE 3.6
Range of VOC Concentrations (μg/L) in 14 NYCDEP Treatment Plants (Summer)

Detected Compounds	Raw Influent	Primary Influent	Primary Effluent	RAS	Aeration Tank	Plant Effluent
1,1,1-Trichloroethane	0.6–2.9	0.6–37.7	0.6–2.9	0.6–1.5	0.6–2.3	0.06–2.6
1.2-Dichloropropane	—	0.2	—	—	—	—
1.4-Dichlorobenzene	0.2	0.2	0.2	—	—	—
1.2-Dichloroethene	—	0.3	0.2	—	—	—
4-Methyl-2-Pentanone	3.0–25.0	2.0–9.0	2.0–9.0	1.0–7.0	1.0–9.0	4.0–17.0
Benzene	0.4–1.8	0.6–8.8	0.4–2.0	0.4–1.8	0.4–2.0	0.4–1.2
Bromodichloromethane	0.3–1.0	0.2–2.0	0.2–0.9	0.2–0.5	0.2–0.7	0.3–0.5
Bromomethane	0.4	—	—	—	—	—
Bromoform	1.0–10.0	2.0–9.0	1.0–10.0	0.3–10.0	0.4–12.0	0.2–32.0
Chloroform	4.5–12.0	6.0–10.5	4.5–12.0	1.4–6.0	1.4–9.0	—
Chloromethane	0.4	0.4–0.5	0.2–0.4	0.2–0.3	0.2–0.3	—
Cis-1.2.Dichloroethene	0.7–6.6	0.7–4.4	0.7–4.4	0.4–1.3	0.4–1.8	0.4–1.5
Dibromodichloromethane	1.0	—	—	—	—	0.3–0.4
Dichlorodifluoromethane	0.2–1.0	—	—	—	—	—
Ethylbenzene	0.2	0.2–0.3	—	—	—	—
Freon Tf	—	—	—	0.3	0.3	0.2
Methylene Chloride	8.4–15.4	5.6–19.6	7.0–16.8	7.0	7.0	7.0–14.0
M&P-Xylene	1.3–46.9	1.3–6.7	1.3–5.4	1.3–3.4	1.3–3.4	2.0–13.4
Naphthalene	0.2–0.4	0.2–0.6	0.2–0.6	0.2	0.2	--
O-Xylene	1.3–26.8	1.3–2.7	1.3–2.7	1.3–2.0	1.3–2.0	1.3
Tetrachloroethene	4.0–60.0	4.0–30.0	2.7–30.0	1.3–14.0	4.0–20.0	4.0–12.0
Toluene	3.3–39.6	6.6–42.9	3.3–36.0	1.3–33.0	1.3–36.3	2.0–33.0
Trichlorethene	1.3–13.4	1.3–13.4	2.7–13.4	6.7	2.7–13.4	6.7
Trichlorofluoromethane	—	—	—	—	3.0	—
Vinyl Chloride	0.3	—	—	—	—	—
Acetone	120.0–330.0	95.0–300.0	99.0–360.0	35.0–270.0	19.0–400.0	44.0–290.0

Source: New York City Department of Environmental Protection, Wastewater Content of Volatile Organic Compounds at the New York City Department of Environmental Protection Water Pollution Control Plants, *Analysis of Volatile Organic Compound Emissions from the New York City Wastewater Collection/Treatment System, Final Report, Vol. I,* Malcolm Pirnie and Illinois Institute of Technology, Chicago, February, 1999.

and hence their emissions. It will be useful for a major municipality to regularly monitor its influent VOC concentrations at least once a month, as is done at the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC), to ensure that the VOC loadings to its treatment facilities are under control. Trends in VOC emissions at the MWRDGC plants are presented in Chapter 15.

3.4 SUMMARY

The main contributing sources of VOCs to a municipality's sewerage system are mainly the water supply, industries and commercial establishments located in the

TABLE 3.7
Statistical Comparison of Detected VOCs in Wastewater for Summer and Winter at 11 Standard Plants

Compound	Raw Influent	Primary Influent	Primary Effluent	RAS	Aeration Pass-B	Aeration Pass-C	Plant Effluent
1,1,1-Trichloroethane	A	A*	A	A	A	R*	A
4-Methyl-2-Pentanone	A	R	R	R	R	R	A
Benzene	R	R	R	R	R	R	R
Bromodichloromethane	R	A*	A*				A
Chloroform	A	A*	A*	A	A	A	R
cis-1,2-Dichloroethene	A	A	A			A	A
M & P Xylenes	A*	R	A*	A	R	R	A
Methylene Chloride	A	A	A	A	A	A	A
Naphthalene	A		A*				
O-Xylene	A*	A	A*				
Tetrachloroethene	A	A	A		R	A	A
Toluene	R	R	R	A*	R	A*	R*
Trichloroethene	A	R*	A	A	A*	A*	A

Source: New York City Department of Environmental Protection, Wastewater Content of Volatile Organic Compounds at the New York City Department of Environmental Protection Water Pollution Control Plants, *Analysis of Volatile Organic Compound Emissions from the New York City Wastewater Collection/Treatment System, Final Report, Vol. I,* Malcolm Pirnie and Illinois Institute of Technology, Chicago, February, 1999.

A: The Null Hypothesis is accepted and there is NOT a statistically significant difference between tests.

R: The Null Hypothesis is rejected and there IS a statistically significant difference between tests.

NA: There is insufficient data (not enough samples) to compute a test statistic.

UNKN: There is sufficient data to compute a test statistic, but not enough to arrive at a conclusion about the Null Hypothesis.

* Indicates t-tests with equal variances. Otherwise, t-tests were computed assuming variances not equal. Levene's test for equality of variances at 0.95 alpha level was used to determine these assumptions.

service area, household and consumer products that find their way into the sewers, surface runoff that occurs during wet weather, and chemical and biogenic reactions that occur during the treatment of water and wastewater.

Neither the same VOCs nor uniformity in their concentration can be expected in wastewater influents because of the high variability associated with industrial, commercial and domestic discharges. Daily, weekly and seasonal variations in VOC concentrations do occur.

TABLE 3.8
Statistical Comparison of Detected VOCs in Wastewater for AM and PM at Three Detailed Plants (Weekday)

Compound	Raw Influent	Primary Influent	Primary Effluent	RAS	Aeration Pass-B	Aeration Pass-C	Plant Effluent
North River							
1,1,1-Trichloroethane	A	A	A	A	A*	A	A
4-Methyl-2-Pentanone	A*	A	A	A	A	A*	A*
Benzene	A	A	A	A	A	A	A*
Bromodichloromethane	A	A	A*	R*	A	A	R
Chloroform	A	A	A	A	A	A	A
cis-1,2-Dichloroethene	A	A	A		A	R	A
m and p Xylenes	A	A	A	A	A	A	A
Methylene Chloride		A*					
o-Xylene	A*	A					
Tetrachloroethene	A	A*	A	A	A	A	A
Toluene	A	A	A	A	A*	A	A*
Rockaway							
4-Methyl-2-Pentanone	A	A	A	A		A	A
Benzene	A	A	A	A	A	A	A
Bromodichloromethane		A*	A			A	A
Bromoform							A
Chloroform	A	A	A	A	A	A	A
cis-1,2-Dichloroethene	A	A	A	A	A	A	A
Dibromochloromethane							A*
m and p Xylenes	A	A			A		
Tetrachloroethene	A	A	A		A		A*
Toluene	A	A	A	A	A	A	A
Trichloroethene	A	A	A*				
Xylene (Total)	A	A*	A	A	A	A*	A
Wards Island							
4-Methyl-2-Pentanone	A*	A	R	A	A	A*	
Benzene	A*	A*	A	A	A	A*	
Bromodichloromethane	A	A				A	
Chloroform	A*	A	A	A	A*	A	
cis-1,2-Dichloroethene	A	A		A	A	A	
Methylene Chloride	A	A		A			
o-Xylene	A						
Tetrachloroethene	A	A			A	R*	
Toluene	R*	R	R	R*	R*	R	
Trichloroethene	R*	R	R*	R*	R*	R	

TABLE 3.8 (CONTINUED)
Statistical Comparison of Detected VOCs in Wastewater for AM and PM at Three Detailed Plants (Weekday)

Source: New York City Department of Environmental Protection, Wastewater Content of Volatile Organic Compounds at the New York City Department of Environmental Protection Water Pollution Control Plants, *Analysis of Volatile Organic Compound Emissions from the New York City Wastewater Collection/Treatment System, Final Report, Vol. I,* Malcolm Pirnie and Illinois Institute of Technology, Chicago, February, 1999.

Notes:

A: Null Hypothesis is accepted and there is NOT a statistically significant difference between tests.

R: The Null Hypothesis is rejected and there IS a statistically significant difference between tests.

NA: There is insufficient data (not enough samples) to compute a test statistic.

UNKN: There is sufficient data to compute a test statistic, but not enough to arrive at a conclusion about the Null Hypothesis.

* Indicates t-tests with equal variances. Otherwise, t-tests were computed assuming variances not equal. Levene's test for equality of variances at 0.95 alpha level was used to determine these assumptions.

TABLE 3.9
Statistical Comparison of Detected VOCs in Wastewater for AM and PM at Three Detailed Plants (Weekend)

Compound	Raw Influent	Primary Influent	Primary Effluent	RAS	Aeration Pass-B	Aeration Pass-C	Plant Effluent
			North River				
1,1,1-Trichloroethane	R	R	R	R	A	A	A*
4-Methyl-2-Pentanone	A	A	A	A	A	A	A*
Benzene	A	A	A	A*	A	A	A
Bromodichloromethane	A	A	A	A	A	A	A
Chloroform	R	A*	A	A	A*	A	A
cis-1,2-Dichloroethene	A	A	A		A*	A*	R
m & p Xylenes	A	R	A	R	A	A	A
o-Xylene	A*						
Tetrachloroethene	R*	R	R	A	A	R*	
Toluene	A	A	A*	A	A	A	A

TABLE 3.9 (CONTINUED)
Statistical Comparison of Detected VOCs in Wastewater for AM and PM at Three Detailed Plants (Weekend)

Compound	Raw Influent	Primary Influent	Primary Effluent	RAS	Aeration Pass-B	Aeration Pass-C	Plant Effluent
			Rockaway				
4-Methyl-2-Pentanone	A	A	A	A		A	
Benzene	A	A	A*	A	R*	A	A*
Bromodichloromethane	A	A	A*			A	A
Bromoform							R*
Chloroform	A	A	A	A	A*	A	A
Chloromethane							
cis-1,2-Dichloroethene	A	A	A	A	A*	A	A
Dibromochloromethane							A
m & p Xylenes		A*	A				
Tetrachloroethene	A	A	A	A	A*	A	A
Toluene	A*	A*	A*	A*	A	A*	A*
Trichloroethene	R*	A	A*				
Xylene (Total)	R*	A	A	A	A	A	A
			Wards Island				
4-Methyl-2-Pentanone	A	A	A	A	A	A	
Benzene	A	A	A*	A	A*	A	
Bromodichloromethane	A	A				A	
Chloroform	A	A	A	A	A*	A	
cis-1,2-Dichloroethene	A	A	A*	A	R		
m & p Xylenes	A*	A			A	A	
Methylene Chloride		A*		A*			
o-Xylene	A						
Tetrachloroethene	A	A*			A	A*	
Toluene	A	A	A	A	A	A	

Source: New York City Department of Environmental Protection, Wastewater Content of Volatile Organic Compounds at the New York City Department of Environmental Protection Water Pollution Control Plants, *Analysis of Volatile Organic Compound Emissions from the New York City Wastewater Collection/Treatment System, Final Report, Vol. I,* Malcolm Pirnie and Illinois Institute of Technology, Chicago, February, 1999.

Notes: See Table 3.8.

TABLE 3.10
Statistical Comparison of Detected VOCs in Wastewater for Summer and Winter at Three Detailed Plants

Compound	Raw Influent	Primary Influent	Primary Effluent	RAS	Aeration Pass-B	Aeration Pass-C	Plant Effluent
			North River				
1,1,1-Trichloroethane	A	A	A	A	R	R	A
4-Methyl-2-Pentanone	A*	R	A	R		R	
Benzene	R	R	R*	R*	R	R	R*
Bromodichloromethane	A	A	A	A	A	R	A
Chloroform	A	R*	R	A	R	R	R
cis-1,2-Dichloroethene	A	A	A		R	A	A
m & p Xylenes	A	R*	A	R	R	R*	A
Methylene Chloride		A					
o-Xylene	A*	A					
Tetrachloroethene	A*	A	A	A	A	A	A
Toluene	A	R	R	R	R	R*	R*
			Rockaway				
Benzene	A	A	A*	A*	A*	A	A*
Bromodichloromethane	A	A					
Chloroform	A	A	A	R*	R	R*	R
cis-1,2-Dichloroethene			A*	R	R	R	A*
Tetrachloroethene	A	R	R	A	A	A	
Toluene	R*	A*	A*	A*	A*	A*	R*
			Wards Island				
4-Methyl-2-Pentanone		A	A	A*	A	A*	A*
Benzene	R*	R*	A*	A	A	A	
Bromodichloromethane		A					
Chloroform	R	A	R		A*	R	
cis-1,2-Dichloroethene	A*	A*					A*
m & p Xylenes	A*	R			R		
Tetrachloroethene	A	A*			A	A	
Toluene	A*	A*	A*	A*	A*	A*	A*

Source: New York City Department of Environmental Protection, Wastewater Content of Volatile Organic Compounds at the New York City Department of Environmental Protection Water Pollution Control Plants, *Analysis of Volatile Organic Compound Emissions from the New York City Wastewater Collection/Treatment System, Final Report, Vol. I,* Malcolm Pirnie and Illinois Institute of Technology, Chicago, February, 1999.

Notes: See Table 3.8.

REFERENCES

1. Lucas, R., Emissions of Potentially Hazardous Air Pollutants from Publicly Owned Treatment Works, Water Pollution Control Federation/U.S. EPA Workshop Report and Proceedings of Air Toxic Emissions and POTWs, Alexandria, Virginia, 1989.
2. ASCE, Water Environment Federation and American Society of Civil Engineers, Toxic Emissions from Wastewater Treatment Facilities, Al Pincince (Ed.), Reston, Virginia, 1995.
3. Noll, K.E. and De Paul, F.T., Emissions of Volatile Organic Compounds from the Sewage Treatment Facilities of the Metropolitan Sanitary District of Greater Chicago, Report to the Metropolitan Sanitary District of Greater Chicago, 1987.
4. Bishop, W., Witherspoon, J., Card, T., Chang, D.P.Y. and Corsi, R., VOC Vapor Phase Control Technology Assessment, WPCF Research Foundation Report 90-2, 1990.
5. Card, T., Volatile organic compound removal in packed towers and atomized mist odor scrubbing systems. Paper presented at the 62nd Annual Water Pollution Control Federation Conference, San Francisco, California, October 1989.
6. Tata, P., Soszynski, S., Lordi, D.T., Zenz, D.R., Lue-Hing, C. and Card, T., Prediction of volatile organic compound emissions from publicly owned treatment works. Paper presented at the 68th Annual Water Environment Federation Conference, Miami Beach, Florida., October 1995.
7. Caballero, R.C. and Griffith, P., VOC emissions for POTWs, Water Pollution Control Federation/U.S. EPA Workshop Report and Proceedings of Air Toxic Emissions and POTWs, Alexandria, Virginia, 1989.
8. Komilis, D.K., Park, J.K. and Ham, R.K., Production of volatile organic compounds during composting of municipal solid wastes, Paper presented at the 1998 Annual Water Environment Federation Conference, Orlando, Florida, October 1998.
9. Lurker, P.A., Clark, C.S. and Elia, V.J., Atmospheric release of chlorinated organic compounds from the activated sludge treatment process, J. Water Poll. Control Fed., 54: 1566, 1982.
10. Lurker, P.A., Clark, C.S., Elia, V.J., Gartside, P.S. and Kinman, R.N., Aerial organic chemical release from activated sludge, Water Res., 18: 489, 1984.
11. Dunovant, V.S., Clark, C.S., Que Hee, S.S., Hertzburg, V.S. and Trapp, J.H., Volatile organic emissions in the wastewater and air spaces of three wastewater treatment plants, J. Water Poll. Control Fed., 58: 886, 1986.
12. Namkung, E. and Rittman, B., Estimating volatile organic compound emissions from publicly owned treatment works, J. Water Poll. Control Fed., 59: 67, 1987.
13. Berglund, L.A. and Whipple, G.M., Predictive modeling of organic emissions, Chem. Eng. Prog., 6, 217, 1987.
14. Ismail, F.T. and Lindstrom, K., Addressing Toxic Air Emissions from California Publicly Owned Treatment Works, Final Report, California State Water Resources Control Board, 1990.
15. Chang, D.P.Y., Schroeder, E.D. and Corsi, R.L., Emissions of Volatile and Potentially Toxic Compounds from Sewage Treatment Plants and Collection Systems, Report to the California Air Resources Board, Contract A5-127-32, July 1987.
16. Levins, P., Sources of Toxic Pollutants Found in Influents to Sewage Treatment Plants, U.S. EPA Report No. 440/4-81/007, 1979.
17. Baillod, C.R., Crittenden, J.C., Mihelcic, J.R., Rogers, T. and Leslie Grady, Jr., Critical Evaluation of the State of Technologies for Predicting the Transport and Fate of Toxic Compounds in Wastewater Facilities, WPCF Research Foundation Project 90-1, December 1990.

18. U.S. EPA, Fate of Priority Pollutants in Publicly Owned Treatment Works, Report 440/1-82-003, 1982.
19. Pellizzari, E.D. and Little, L, Collection and Analysis of Purgeable Organics Emitted from Wastewater Treatment Plants, U.S. EPA Report No. 600/2-80-017, March 1980.
20. Bell, J.P., Osinga, I. and Melcer, H., Investigation of Stripping of Volatile Organic Contaminants in Municipal Wastewater Treatment Systems — Phase I, Ontario Ministry of the Environment, Toronto, 1988.
21. Hellier, W.G., EBMUD monitoring program of air toxics emissions, Workshop Report and Proceedings of Air Toxic Emissions and POTWs, Water Pollution Control Federation/U.S. EPA, Alexandria, Virginia, 1989.
22. New York City Department of Environmental Protection, Wastewater Content of Volatile Organic Compounds at the New York City Department of Environmental Protection Water Pollution Control Plants, *Analysis of Volatile Organic Compound Emissions from the New York City Wastewater Collection/Treatment System, Final Report, Vol. I,* Malcolm Pirnie and Illinois Institute of Technology, Chicago, February, 1999.

4 Source Characterization and VOCs of Importance

Tom Card, Prakasam Tata, Cecil Lue-Hing and Jay Witherspoon

CONTENTS

4.1 Introduction 59
4.2 Collection Systems 59
4.3 POTWs 60
  4.3.1 Preliminary/Primary Treatment 61
  4.3.2 Biological Treatment 61
  4.3.3 Post-Biological Treatment 62
  4.3.4 Solids Handling 62
  4.3.5 Combustion Sources 62
4.4 Selection of Important VOCs 62
  4.4.1 Recommended Classification Strategy 63
  4.4.2 Compound Group 1: Volatile and Degradable Compound 66
  4.4.3 Compound Group 2: Volatile and Nondegradable Compounds 66
  4.4.4 Compound Group 3: Nonvolatile and Degradable Compounds 66
  4.4.5 Compound Group 4: Nonvolatile and Nondegradable Compounds 67
  4.4.6 Compound Group 5: Total Hydrocarbons 67
4.5 Other Characterization Data 67
  4.5.1 1990 Clean Air Act Amendments Title III List 67
  4.5.2 Synthetic Organic Chemical Manufacturing Industry (SOCMI), Hazardous Organic NESHAP (HON) List (40 CFR Part 63) 67
  4.5.3 AMSA List 67
4.6 Summary 69
References 71

4.1 INTRODUCTION

This chapter presents a brief overview of POTW processes, as well as a general discussion on characterization and classification of VOCs. It is important to understand

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

the basic principles of wastewater collection and treatment before considering the complexities of air emission characterization. The overview of collection systems and wastewater treatment processes is intended to serve as an introduction, primarily for air quality specialists who may have limited knowledge of wastewater treatment. Hence, this overview does not thoroughly address the various aspects of design, operation and performance of different collection systems and POTW components. Details pertaining to design and various components of typical collection systems and POTW unit processes are found in standard reference books.[1–3]

VOC characterization and classification are described in the context of three California efforts: the Tri-TAC VOC characterization/control document,[4] the Joint Emissions Inventory Program (JEIP)[5] and the Pooled Emissions Estimation Program (PEEP).[6]

4.2 COLLECTION SYSTEMS

A collection system consists primarily of sewers that collect and transport wastewater generated from various sources in a community to a treatment facility. Three types of collection systems have been developed: (1) sanitary, (2) stormwater and (3) combined, which transports both the sanitary and stormwater discharges either separately or in a combined manner. Most sewer systems are constructed under ground. Sewer systems typically consist of trunk sewers that discharge wastewater to POTWs for treatment. These sewers are connected to branch sewer lines that intercept and receive sewage from lateral sewers that collect wastewater discharged from residential and industrial and other commercial entities located in a POTW service area. A typical collection system consists of the following major components:

- Sewers (e.g., trunk, interceptor and lateral)
- Appurtenances (e.g., lift/pumping stations, drop shafts, junction boxes and sumps, manholes and inverted siphons or drop sewers)

4.3 POTWs

POTWs can have various unit processes of different designs. However, the unit processes used at POTWs generally have similar functions. Figure 4.1 presents a generalized process flow schematic for a POTW. As shown in the figure, POTW unit processes that handle liquid and solid streams can be divided into four basic categories. Preliminary/primary treatment processes are employed to achieve physical separation of the solids and other phases (oil and grease) that can be easily removed from the liquid phase. These processes typically employ screening grit removal, settling and skimming. Aerobic biological treatment processes usually follow the preliminary and primary treatment units and are typically used to further remove colloidal and dissolved organic matter from the liquid stream through microbial degradation of dissolved organic material in the liquid. Post-biological treatment processes are used when high levels of treatment are required. Post-biological treatment can include additional biological and other physicochemical processes (e.g., nitrification and denitrification filtration, carbon adsorption and disinfection).

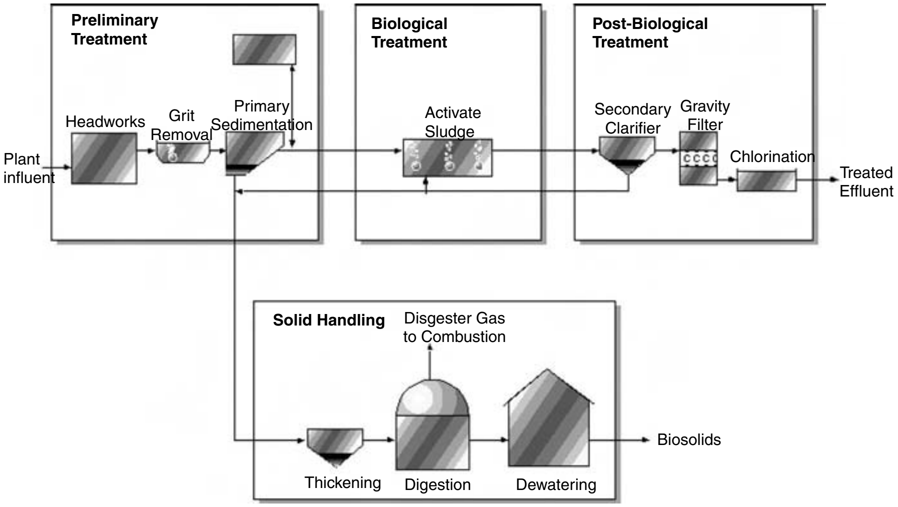


FIGURE 4.1. Typical POTW process schematic.

Finally, solids handling unit processes are used to further treat the solids materials removed during liquid treatment. Solids processes include thickening, dewatering, aerobic digestion, anaerobic digestion and incineration.

The degree of air emissions from each unit process of a typical POTW as shown in Figure 4.1 is impacted by the processes upstream and downstream of it, creating a potentially complex and interrelated cause and effect situation within the POTW. For example, covering a preliminary/primary treatment process will likely cause VOCs to be contained and, to some extent, remain in solution. This creates the potential for greater emissions from subsequent downstream processes.

To estimate air emissions from wastewater treatment processes, they have been grouped into the following five categories based on their typical emission mechanisms and operational characteristics.

4.3.1 PRELIMINARY/PRIMARY TREATMENT

Preliminary/primary treatment consists of the following components:

- Headworks
- Aerated grit and channels
- Primary sedimentation
- Flow equalization

4.3.2 BIOLOGICAL TREATMENT

Biological wastewater treatment systems consist of the following:

- Diffused air activated sludge

- Mechanically aerated activated sludge
- High purity oxygen activated sludge
- Attached media reactors (e.g., trickling filters and rotating biological contactors)

4.3.3 POST-BIOLOGICAL TREATMENT

Post-biological treatment units of a typical POTW consist of the following:

- Secondary clarifiers
- Effluent filtration
- Chlorination

4.3.4 SOLIDS HANDLING

The solids handling unit processes in a POTW may consist of enclosed or open solids-handling facilities, including:

- Dissolved air flotation thickening
- Aerobic digestion
- Anaerobic digestion
- Dewatering
- Additional stabilization (e.g., composting, lime addition, etc.)
- Miscellaneous processes
- Lagooning
- Drying (e.g., air, heat drying, etc.)
- Storage

4.3.5 COMBUSTION SOURCES

POTWs consist of other processes that include:

- Internal combustion engines
- Boilers
- Flares
- Incinerators

For each of the above process groups, a discussion on the description of the unit process, emission mechanism and key factors affecting emission is included in Chapter 5. Emissions from collection systems are further addressed in Chapters 5 and 6.

4.4 SELECTION OF IMPORTANT VOCs

In 1987, California passed a state law that required the characterization of air toxic compounds from a variety of industrial and public sources. To respond to that law and additional local laws, a consortium of communities in the San Francisco Bay

Area funded a project to develop a VOC characterization and control guidance document for POTWs.[4]

One of the goals in developing the Tri-TAC BACT Guidance Document[4] was to provide a simple and efficient method of making BACT determinations for POTWs. The first step in making that determination is to ascertain the probable air stream composition. The many techniques for undertaking this are mostly very time consuming and expensive. However, sufficient influent VOC concentration information is currently available to make a close approximation of total VOC emissions. This section describes the default method for quickly determining the probable air stream composition.

The Tri-TAC BACT Guidance Document is concerned with both toxic and hydrocarbon emissions. Currently, more than 600 air toxic compounds have been identified Since it is not possible to track all 600, a methodology was developed for quickly estimating the air stream composition of groups of these compounds. In addition, to efficiently arrive at a first estimate of compound concentrations for BACT determination, it is important to have as few groups of these compounds as possible. This chapter presents the methodology used to select five groups of compounds that will allow rapid estimation of gas phase concentrations. The speciation (of both mass and toxicity) of these groups can be estimated by using the provided mass (and toxicity) distribution. This grouped method may not be appropriate for all BACT determinations and more-sophisticated methods may be required for a more detailed analysis. Many wastewater facilities have paid between $100,000 and $500,000 for accurate air emissions speciations that are unique to their facilities.

Of the 600 or so identified toxic compounds mentioned previously, nine account for over 99% of the source toxicity. These compounds and their proportional contribution to source toxicity are shown in Figure 4.2. Of the nine compounds, only four are associated with emissions from non-combustion processes — chloroform, benzene, methylene chloride and tetrachloroethene. Figures 4.3 and 4.4 show the relative mass emissions and source toxicity contribution for these compounds. All toxicity values used were the official State of California values as of 1993.

Less is known about hydrocarbon emissions than toxic emissions. For most jurisdictions, only photoreactive hydrocarbons are of concern. These include all gas-phase organic compounds except methane, freons and some chlorinated hydrocarbons. The majority of hydrocarbon compounds released at wastewater treatment facilities are compounds with lower partition constants (less than 0.01 milligram per liter [mg/l]), such as ethanol and acetone, or compounds that are more volatile, but highly sorbed onto wastewater solids, like tri-methyl benzene. Figure 4.5 presents a summary of the preliminary JEIP[5] data showing the fate of hydrocarbons in typical wastewater treatment facilities. Very little of the total hydrocarbon mass is volatilized, with most of it leaving the liquids treatment train sorbed onto the wastewater solids.

4.4.1 RECOMMENDED CLASSIFICATION STRATEGY

The volatilization of compounds from liquid surfaces is controlled by Equation 4.1:

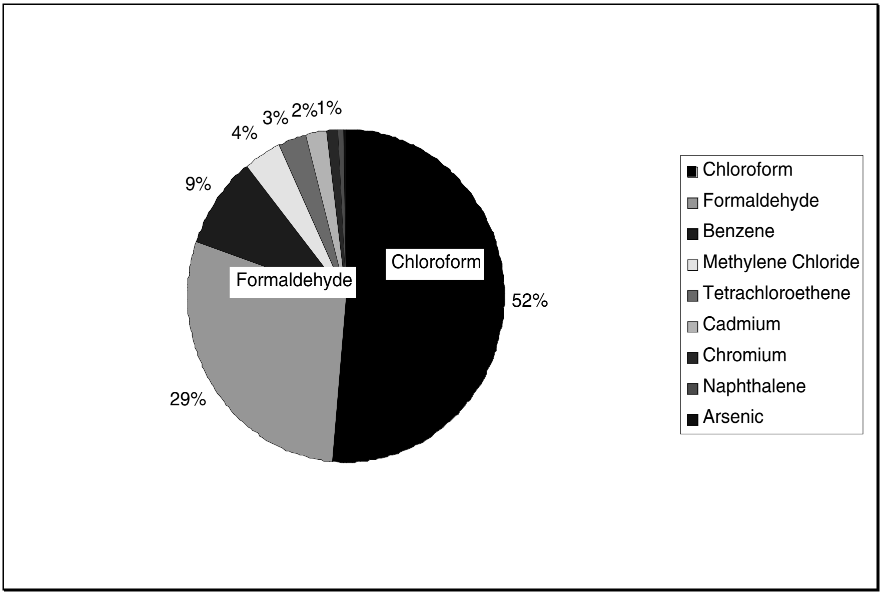


FIGURE 4.2 Relative contribution to total source toxicity of the major toxic compounds.

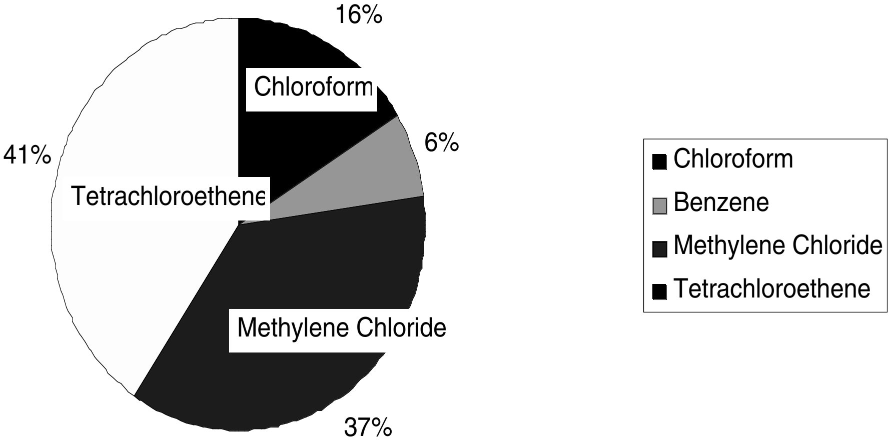


FIGURE 4.3 Flow weighted average influent liquid phase mass loading of the major toxics.

$$R_v = -\left(\frac{C_l - \frac{C_g}{H_c}}{\frac{1}{K} + \frac{1}{H_c K_g}} \right) A \tag{4.1}$$

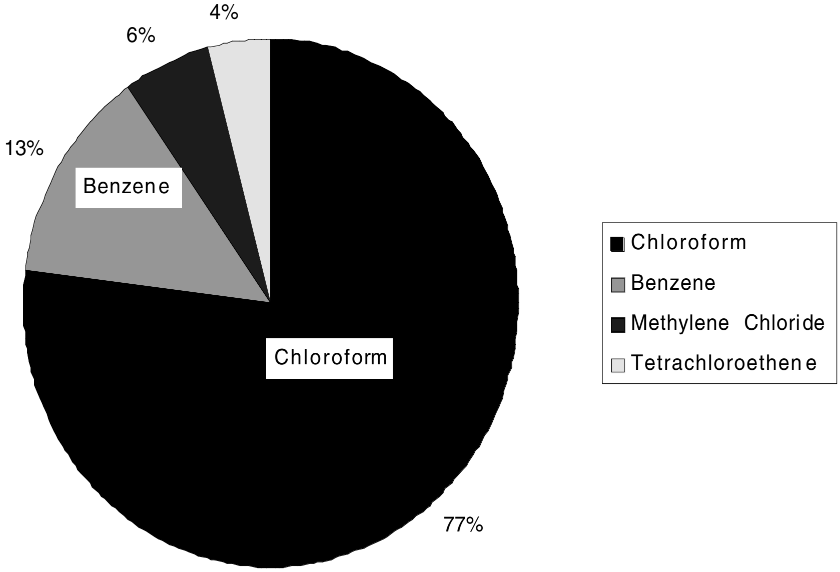


FIGURE 4.4 Flow weighted average toxicity contribution for liquid processes.

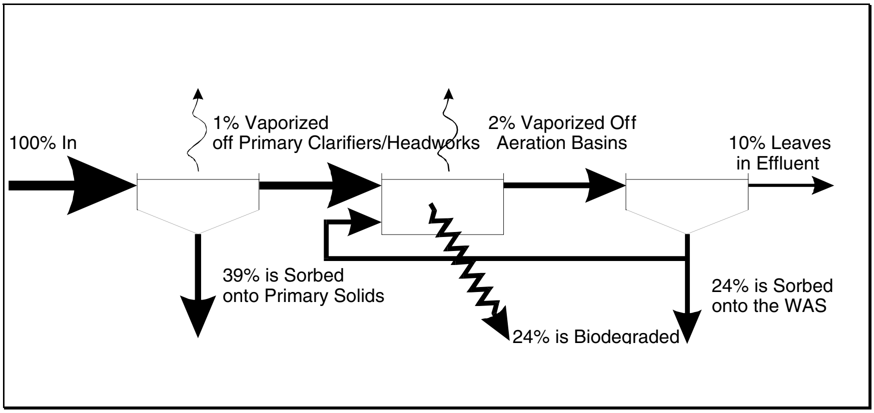

100% In
1% Vaporized off Primary Clarifiers/Headworks
2% Vaporized Off Aeration Basins
10% Leaves in Effluent
39% is Sorbed onto Primary Solids
24% is Biodegraded
24% is Sorbed onto the WAS

FIGURE 4.5 Preliminary joint emissions inventory program total hydrocarbon fate results.

where R_v is the mass rate of volatilization (mg/s), C_l is the aqueous concentration of the compound in question (mg/m^3), C_g is the gas phase concentration (mg/m^3), H_c is the partition coefficient (Henry's Law coefficient, mg/l per mg/l), K_l is the liquid phase mass transfer resistance coefficient (m/s), K_g is the gas phase mass transfer resistance coefficient (m/s) and A is the interfacial surface area (m^2).

Equation 4.1 shows that, for liquid phase controlled compounds, i.e., partition coefficients over 0.01 mg/l per mg/l, the emission rate is a function of the mass transfer coefficient and surface area only when the compounds are not near saturation conditions. Therefore, the emission rate differences for compounds are solely a function of mass transfer coefficients such as Henry's law coefficient, which is a function of liquid phase diffusion rates.

Using the above information, a classification system can be developed based on four toxic compound groups plus one group for total hydrocarbons. Two of the recommended groups are similar to the groups used in extrapolating emission factors in the PEEP,[6] i.e., degradable and nondegradable (or chlorinated and nonchlorinated in PEEP). The other two groups are more specific to hydrocarbon emissions; they are nonvolatile, degradable and nondegradable.

4.4.2 COMPOUND GROUP 1: VOLATILE AND DEGRADABLE COMPOUNDS

These compounds are relatively volatile (partition coefficients above 0.01 mg/l per mg/l) and are readily degradable. Examples include benzene, toluene and xylenes. The emission of these compounds is almost always liquid phase controlled. Therefore, the emission rate differences are determined solely by diffusion rate differences, until saturation conditions are approached. These diffusion rate differences are quite small. The indicator compound that will be used is benzene. If a more accurate estimate is needed for a specific compound, it is recommended that the estimate be based on diffusion rate differences for well-ventilated systems and based on Henry's Law coefficients for poorly ventilated systems. Furthermore, for biological treatment systems, consideration also needs to be made for biodegradability differences.

4.4.3 COMPOUND GROUP 2: VOLATILE AND NONDEGRADABLE COMPOUNDS

These compounds have the same volatilization characteristics as Group 1, but will not significantly degrade in biological treatment systems. Examples include most of the chlorinated hydrocarbons, such as chloroform, trichloroethene, tetrachloroethene and methylene chloride. Emission rates of these compounds can be estimated based on the same techniques described for Group 1.

4.4.4 COMPOUND GROUP 3: NONVOLATILE AND DEGRADABLE COMPOUNDS

With the exception of tri-methyl benzene, the vast majority of compounds associated with hydrocarbon emissions fits in this category. Based on preliminary JEIP data, typical emission factors for most processes are around 1% for these compounds; aeration basins emit about 2%. Typical compounds include acetone, limonene and alcohols. Other emission rates of these compounds can be estimated based on Henry's Law coefficient differences.

4.4.5 COMPOUND GROUP 4: NONVOLATILE AND NONDEGRADABLE COMPOUNDS

Based on the preliminary JEIP[5] data, it appears that about 10% of the influent hydrocarbons meet this category. At this time, compounds included in this group and their specific properties are unknown. However, the group is included because it is anticipated that subsequent JEIP events will provide more information on these compounds.

4.4.6 COMPOUND GROUP 5: TOTAL HYDROCARBONS

Little is known about the behavior of the bulk hydrocarbon fraction. However, the JEIP[5] data can be used to estimate gas phase concentrations for this group.

4.5 OTHER CHARACTERIZATION DATA

The following sections present lists of general air toxic compounds and some that have been specifically developed for POTWs or industrial wastewater treatment.

4.5.1 1990 CLEAN AIR ACT AMENDMENTS TITLE III LIST

The 1990 CAAA stipulated a list of the following compounds to be classified as air toxic compounds and presented them in Title III of these amendments. This list is presented in Chapter 2, U.S. Air Quality Regulations.

4.5.2 SYNTHETIC ORGANIC CHEMICAL MANUFACTURING INDUSTRY (SOCMI), HAZARDOUS ORGANIC NESHAP (HON) LIST (40 CFR PART 63)

The 1990 CAAA list was further refined to compounds that could be found in the liquid phase and could volatilize for developing a rule for the SOCMI HON developed in the early 1990s. This list also includes the EPA opinion as to the typical fraction emitted (Fr) from wastewater treatment for each compound. This list and the Fr Values for various compounds are presented in Table 4.1.

4.5.3 AMSA LIST

Based on the above data, AMSA conducted a survey of several POTWs of different sizes and reported the following list of compounds (Table 4.2) that were detected in the influents of the POTWs.

Based on the data presented, very few compounds are shown to be of general concern for air toxic emissions from the liquid processes at POTWs. The first ten compounds in Table 4.2 represent over 90% of the emissions mass from POTWs in the United States. The remaining compounds can be of concern in specialized cases. Note that this does not address emissions from combustion sources. The combustion source emissions need to be addressed based on known emissions from each type of source.

TABLE 4.1
Organic HAPS Subject to the Wastewater Provisions of the SOCMI HON

Chemical Name	CAS No.	Fr
Acetaldehyde	75070	0.95
Acetonitrile	75058	0.62
Acetophenone	98862	0.72
Acrolein	107028	0.96
Acrylonitrile	107131	0.96
Allyl chloride	107051	0.99
Benzene	71432	0.99
Benzyl chloride	100447	0.99
Biphenyl	92524	0.99
Bromoform	75252	0.99
Butadiene (1,3-)	106990	0.99
Carbon disulfide	75150	0.99
Carbon tetrachloride	56235	0.99
Chlorobenzene	108907	0.99
Chloroform	67663	0.99
Chloroprene (2-Chloro-1,3-butadiene)	126998	0.99
Cumene	98828	0.99
Dichlorobenzene (p-)	106467	0.99
Dichloroethane (1,2-) (Ethylene dichloride)	107062	0.99
Dichloroethyl ether (Bis(2-chloroethyl)ether)	111444	0.87
Dichloropropene (1,3-)	542756	0.99
Diethyl sulfate	64675	0.90
Dimethyl sulfate	77781	0.53
Dimethylaniline (N,N-)	121697	0.99
Dimethylhydrazine (1,1-)	57147	0.57
Dinitrophenol (2,4-)	51285	0.99
Dinitrotoluene (2,4-)	121142	0.38
Dioxane (1,4-) (1,4-Diethyleneoxide)	123911	0.37
Epichlorohydrin(1-Chloro-2,3-epoxypropane)	106898	0.91
Ethyl acrylate	140885	0.99
Ethylbenzene	100414	0.99
Ethyl chloride (Chloroethane)	75003	0.99
Ethylene dibromide (Dibromomethane)	106934	0.99
Ethylene glycol dimethyl ether	110714	0.90
Ethylene glycol monobutyl ether acetate	112072	0.76
Ethylene glycol monomethyl ether acetate	110496	0.28
Ethylene oxide	75218	0.98
Ethylidene dichloride (1,1-Dichloroethane)	75343	0.99
Hexachlorobenzene	118741	0.99
Hexachlorobutadiene	87683	0.99
Hexachloroethane	67721	0.99
Hexane	110543	0.99
Isophorone	78591	0.60

TABLE 4.1 (CONTINUED)
Organic HAPS Subject to the Wastewater Provisions of the SOCMI HON

Chemical Name	CAS No.	Fr
Methanol	67561	0.31
Methyl bromide (Bromomethane)	74839	0.99
Methyl chloride (Chloromethane)	74873	0.99
Methyl ethyl ketone (2-Butanone)	78933	0.95
Methyl isobutyl ketone (Hexone)	108101	0.99
Methyl methacrylate	80626	0.98
Methyl tert-butyl ether	1634044	0.99
Methylene chloride (Dichloromethane)	75092	0.99
Naphthalene	91203	0.99
Nitrobenzene	98953	0.80
Nitropropane (2-)	79469	0.98
Phosgene	75445	0.99
Propionaldehyde	123386	0.99
Propylene dichloride (1,2-Dichloropropane)	78875	0.99
Propylene oxide	75569	0.99
Styrene	100425	0.99
Tetrachloroethane (1,1,2,2-)	79345	0.99
Tetrachloroethylene (Perchloroethylene)	127184	0.99
Toluene	108883	0.99
Toluidine (o-)	95534	0.44
Trichlorobenzene (1,2,4-)	120821	0.99
Trichloroethane (1,1,1-) (Methyl chloroform)	71556	0.99
Trichloroethane (1,1,2-) (Vinyl trichloride)	79005	0.99
Trichloroethylene	79016	0.99
Trichlorophenol (2,4,5-)	95954	0.96
Triethylamine	121448	0.99
Trimethylpentane (2,2,4-)	540841	0.99
Vinyl acetate	108054	0.99
Vinyl chloride (Chloroethylene)	75014	0.99
Vinylidene chloride (1,1-Dichloroethylene)	75354	0.99
Xylene (m-)	108383	0.99
Xylene (o-)	95476	0.99
Xylene (p-)	106423	0.99

Source: 40 CFR Part 63, NESHAP(HON) List

TABLE 4.2
AMSA Recommended Air Toxic Compound List for POTWs

CAS	Chemical Name	OAQPS Conc. µg/l	AMSA Conc. µg/l	OAQPS Emission Factor	OAQPS Emissions #/yr/MGD	AMSA Emissions #/yr/MGD
1330207	Xylenes (isomers and mixture)		20.99	0.3466		22.16
75092	Methylene chloride (Dichloromethane)	109.00	10.92	0.4765	158.20	15.85
108101	Methyl isobutyl ketone (Hexone)		111.42	0.0445		15.09
127184	Tetrachloroethylene (Perchloroethylene)	25.70	8.46	0.5493	43.00	14.15
108883	Toluene	203.00	14.97	0.2764	170.90	12.60
71556	Methyl chloroform (1,1,1 Trichloroethane)	54.70	4.63	0.7023	117.00	9.90
67663	Chloroform	66.60	5.90	0.4196	85.12	7.54
107028	Acrolein	0.01	41.86	0.0311	0.00	3.97
71432	Benzene (including benzene from gasoline)	124.00	3.09	0.4167	157.38	3.92
106467	1,4 Dichlorobenzene(p)	7.75	6.97	0.1574	3.72	3.34
100414	Ethyl benzene	128.00	2.55	0.3529	137.57	2.74
79016	Trichloroethylene	23.90	1.44	0.6008	43.73	2.64
100425	Styrene		1.19	0.5717		2.07
78933	Methyl ethyl ketone (2-Butanone)		12.26	0.0533		1.99
108907	Chlorobenzene	0.04	3.38	0.1869	0.02	1.92
75354	Vinylidene chloride (1,1-Dichloroethylene)	0.27	0.80	0.7047	0.57	1.72
91203	Naphthalene	45.00	1.79	0.0875	11.99	0.48
107062	Ethylene dichloride (1,2-Dichloroethane)	2.37	0.59	0.2222	1.60	0.40
107131	Acrylonitrile		3.18	0.0353		0.34
56235	Carbon tetrachloride	5.21	0.06	0.7446	11.82	0.14
75014	Vinyl chloride	2.10	0.02	0.9735	6.23	0.06
117817	Bis(2 ethylhexyl) phthalate (DEHP)	44.90		0.0001	0.01	
542881	Bis(chloromethyl)ether	0.02		0.0058	0.00	
75252	Bromoform	0.00		0.1183	0.00	
67561	Methanol			0.0079		
84742	Dibutylphthalate	0.85		0.0000	0.00	
111444	Dichloroethyl ether (Bis(2-chloroethyl)ether)	0.02		0.0058	0.00	
131113	Dimethyl phthalate	0.05		0.0005	0.00	
123911	1,4-Dioxane (1,4-Diethyleneoxide)				0.00	

TABLE 4.2 (CONTINUED)
AMSA Recommended Air Toxic Compound List for POTWs

CAS	Chemical Name	OAQPS Conc. µg/l	AMSA Conc. µg/l	OAQPS Emission Factor	OAQPS Emissions #/yr/MGD	AMSA Emissions #/yr/MGD
106934	Ethylene dibromide (Dibromoethane)				0.00	
67721	Hexachloroethane	0.00		0.3654	0.00	
74839	Methyl bromide (Bromomethane)	0.02		0.9857	0.06	
74873	Methyl chloride (Chloromethane)	0.71		0.5542	1.19	
98953	Nitrobenzene	0.11		0.0176	0.01	
87865	Pentachlorophenol	4.49		0.0134	0.18	
108952	Phenol	1440.00		0.0009	4.10	
1336363	Polychlorinated biphenyls (Aroclors)	0.02	0.0003	0.00		
78875	Propylene dichloride (1,2 Dichloropropane)	0.00		0.2602	0.00	
79345	1,1,2,2 Tetrachloroethane	0.02		0.1020	0.01	
120821	1,2,4 Trichlorobenzene	0.02		0.0670	0.00	
79005	1,1,2 Trichloroethane	7.16		0.1498	3.27	
88062	2,4,6 Trichlorophenol	0.89		0.0083	0.02	
	Sum	2296.92	256.47		957.71	123.02
	Plant Wide Emission Factor				42%	48%
	Flow Cutoff for Major Source (MGD)				52.21	406.44

Source: Unpublished survey results of the Association of Metropolitan Sewerage Agencies

4.6 SUMMARY

Characterization of VOCs at POTWs is complex because of the varying nature of collection systems and wastewater treatment processes. The degree of air emissions from each unit process of a typical POTW is impacted by the process upstream and downstream of it, creating a potentially complex and interrelated cause and effect situation within the POTW.

Important work has been done to identify VOCs of importance. Three efforts of note were conducted in California: the Tri-TAC Guidance Document,[4] the JEIP[5] and the PEEP.[6] Other important information sources are the CAAA Title III list, the SOCMI HON list and the AMSA list.

REFERENCES

1. Metcalf and Eddy, Inc., *Wastewater Engineering: Collection and Pumping of Wastewater*, McGraw-Hill, New York, 1981.
2. Viessman, W. Jr. and Hammer, M.J., *Water Supply and Pollution Control, 6th Edition*, Addison Wesley, Menlo Park, California, 1998
3. Fair, G.M. and Geyer, J.C. , *Water Supply and Wastewater Disposal*, John Wiley & Sons, New York, NY, 1961.
4. Tri-TAC., Guidance Document on Control Technology for VOC Air Emissions from POTWs, 1994.
5. SCAQMD Rule 1179, Emissions Inventory Report for JEIP Participating Agencies, Joint Emissions Inventory Program (JEIP) Report, CH2M HILL, Oakland, California, 1993.
6. Pooled Emission Estimation Program, Final Report for Publicly Owned Treatment Works (POTWs), J.M. Montgomery Consulting Engineers, Pasadena, California, 1990.

5 Unit Processes and Emissions: An Overview

Jay Witherspoon, William Desing and Prakasam Tata

CONTENTS

5.1 Introduction 74
5.2 Collection Systems 74
  5.2.1 Process Description of Collection Systems 74
  5.2.2 Emission Mechanisms of Collection Systems 75
  5.2.3 Key Factors Affecting Emissions of Collection Systems 76
5.3 Preliminary/Primary Treatment 77
  5.3.1 Process Description for Preliminary/Primary Treatment 77
  5.3.2 Emission Mechanisms for Preliminary/Primary Treatment 78
  5.3.3 Key Factors Affecting Emissions from Preliminary/Primary Treatment 79
5.4 Biological Treatment 79
  5.4.1 Process Description of Biological Treatment 80
  5.4.2 Emission Mechanisms for Biological Treatment 81
  5.4.3 Key Factors Affecting Emissions for Biological Treatment 81
5.5 Post-Biological Treatment 82
  5.5.1 Process Description for Post-Biological Treatment 82
  5.5.2 Emission Mechanisms for Post-Biological Treatment 83
  5.5.3 Key Factors Affecting Emissions for Post-Biological Treatment 84
5.6 Solids Handling 85
  5.6.1 Process Description for Solids Handling 86
  5.6.2 Emission Mechanisms for Solids Handling Processes 87
  5.6.3 Key Factors Affecting Emissions for Solids Handling 88
5.7 Combustion Processes 88
  5.7.1 Process Description for Combustion Processes 88
    5.7.1.1 Internal Combustion Engines 89
    5.7.1.2 Flares 89
    5.7.1.3 Boilers 89
    5.7.1.4 Incinerators 89
  5.7.2 Emission Mechanisms for Combustion Processes 90

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

5.7.2.1 VOCs 90
5.7.2.2 Oxides of Nitrogen 90
5.7.2.3 Carbon Monoxide 90
5.7.2.4 Hydrocarbons 90
5.7.2.5 Oxides of Sulfur 90
5.7.2.6 Particulates and Metals 91
5.7.3 Products of Incomplete Combustion 91
5.7.4 Key Factors Affecting Emissions for Combustion Processes 91
5.8 Estimating Emissions from POTWs 91
5.9 Summary 94
References 95

5.1 INTRODUCTION

Proper characterization of emission sources is important because emission levels from these sources, if exceeded beyond specific limits, are used to trigger certain regulatory requirements. These requirements may result in a need for emission controls and operating and construction permits. Characterizing emissions from POTW processes is almost always required as part of the process for obtaining an air permit. Chapter 2 discusses in detail the regulatory requirements such as permitting that may require emission characterization. Proper characterization of air emissions is also important for selecting appropriate air emission control technologies. This chapter provides guidance on characterization of emissions from several POTW emission sources, highlights their predominant emission mechanisms and identifies key factors that affect emissions under the following headings:

Process Description. A brief description of the function of typical facilities is included for each treatment process. In some cases, individual processes with similar characteristics are combined into process groups to facilitate analysis.

Emission Mechanisms. Descriptions of the principal mechanisms responsible for air emissions are presented. Where more than one mechanism is applicable, a discussion of their relative importance is included.

Key Factors Affecting Emissions. Based on the previous description of emission mechanisms for each unit process, key factors affecting emissions are identified; these include design and operational characteristics.

Measurement of Emissions. A brief summary of modeling and other ways to measure emissions is provided. More detailed discussions on how the models are used are provided in subsequent chapters.

5.2 COLLECTION SYSTEMS

5.2.1 Process Description of Collection Systems

Collection systems comprise a network of sewers and other appurtenances that collect and transport wastewater to POTWs for treatment. The nature and magnitude of VOC emissions from collection systems in the POTW service area depend mainly on three factors: the types and concentration of the VOCs discharged into the collection system hydraulic features and ventilation occurring in the collection system. Emissions of VOCs from collection systems have not been extensively studied and are limited to studies reported by a few select investigators. The reported work presented in Chapter 6 indicates that a great deal more study needs to be conducted to clearly understand and validate the nature and magnitude of the emissions from sewers in the United States.

As described in Metcalf and Eddy,[1] several collection systems consist of the following components:

- Lateral sewers (i.e., sewers connected to residential and commercial operations)
- Interceptor sewers (i.e., sewers that intercept and collect sewage from lateral sewers)
- Trunk sewers (i.e., the main sewers that transport sewage to a POTW and are intended to carry the maximum dry weather flow or as much combined sewage as practicable)
- Pumping and lift stations
- Manholes, drop manholes (drop inlets), building connections and flushing devices
- Street inlets and catch basins
- Junction boxes (i.e., where one or more branch sewers join)
- Inverted siphons (depressed sewers) (i.e., a dip or sag introduced into a sewer to pass under a subway or underpass, usually consisting of a number of pipes to handle minimum and maximum dry weather flows as well as storm flows in excess of the dry weather flows)
- Drop shafts (i.e., shafts that discharge wastewater flowing in small surface sewers to larger trunk and intercepting sewers and energy dissipaters to avoid turbulent conditions at the point of entry (most commonly used for small sewers)
- Overflow and diversion structures (i.e., structures used to divert excess flows during wet weather, including different types of weirs and relief siphons)
- Regulating devices (i.e., overflow structures to regulate or divert excess combined sewer flow during wet weather into a relief sewer or devices to control the rate of flow to the interceptor from a combined sewer, including the reverse taintor gate, tipping plate regulator and the hydrobrake
- Outfalls or outlets (i.e., the outlet or the end where wastewater is discharged)

5.2.2 EMISSION MECHANISMS OF COLLECTION SYSTEMS

Sewers are primarily conveyance structures to carry wastewater to POTWs for treatment. Emissions of VOCs occur mainly by volatilization in sewer reaches and at structures where turbulence results from mixing and high velocities. Locations where

VOC volatilization is most likely to occur include sumps into which wastewater drops, drop manholes, pump stations, or when pump discharges occur. Volatilization occurs due to VOC mass transfer from the liquid to gas phase. Sewer ventilation is an important factor and volatilization losses of a VOC via ventilation are proportional to its Henry's law coefficient and ventilation rate because they influence the driving force from the liquid surface to the gaseous phase. At infinite dilution, it is theoretically possible to have a zero concentration of VOCs in the headspace.

Gas–liquid mass transfer occurs primarily at two locations in municipal sewers — along reaches where near-uniform flow conditions prevail and at locations where there is a rapid change of energy from either potential to kinetic or kinetic to potential. Such rapid changes occur in drop manholes, drops into wetwells, hydraulic jumps and pump discharges, etc.

5.2.3 Key Factors Affecting Emissions of Collection Systems

Several factors influence the ventilation and hence the volatilization of VOCs in sewers.[2,3] These include:

- Drag force at the air–wastewater interface
- Barometric pressure gradient
- Eduction by wind
- Buoyancy due to temperature difference
- Breathing loss due to change in liquid level
- Forced ventilation
- Thermal differential

In sewers where sewage flows continuously, liquid drag force also occurs continuously and affects the movement of the headspace gases in the same direction as the liquid flow unless there is a pressure build-up in the sewers (i.e., when the sewer system is tightly closed and there are few openings on the sewer reach). Therefore, the number of openings on the sewer reaches influences the ventilation rate. Also, the gas flow rate in a sewer is influenced by the unwetted surface area of a sewer and the interfacial surface area between the wastewater and overlaying gases.[4,5] The studies conducted by Thistlethwayte[6] and Pescod and Price estimated that as high as 20 turnovers per day can be caused by liquid drag in sewer reaches when there is little resistance to air inflow and exhaust. This rate can drop to as low as one turnover in long sewer reaches (e.g., about 10 miles).

Barometric pressure gradients of 1 millibar per kilometer (mb/km) can lead to ventilation factors that are greater than other factors affecting ventilation in sewers.[4] At a pressure gradient of 1 mb/km, maximum ventilation rates were in the range of one to five turnovers per day in a sewer reach with a very low resistance to air flow; such conditions exist in sewers with many openings. Low turnovers of air occur in pipes with less than 0.3 meters (m) in diameter and high turnovers occur in pipes having a diameter > 1.0 m. At higher pressure gradients and shorter sewer reaches, higher ventilation rates were predicted than longer sewer reaches with lower pressure gradients. This occurs partly due to increased sewer volume as the length of the sewer reach increases while the flow rate remains constant at a fixed value.[4]

Eduction of wind can also affect emissions of VOCs from sewers. It can be caused by a small pressure difference between the sewer pipe and the ambient atmosphere immediately above the manhole covers or house vents when wind blows across them. This pressure difference provides the driving force for volatilization of VOCs contained in the sewage flowing in the sewer. Pressure drops can be high when wind speeds increase and are over house vents, thereby causing higher VOC losses due to the higher eduction of wind that occurs under such conditions. Headspace gas turnover rates due to eduction caused by wind were reported to be 0.09 and 0.13 turnovers per day, respectively, in sewers with a diameter of 1.5 and 0.45 meters.[4]

Using large fans, forced ventilation can be created at specific locations of a collection system to ensure safety of workers when they enter manholes or work near lift stations and deep intake wells. Continuous ventilation is forced along sewer reaches having a low slope. Forced ventilation rates of 25 to 50 turnovers per day were reported in large-diameter interceptors over a distance of about 25 miles.[7]

Changes in liquid flow levels due to variable sewage flow rates cause inversely proportional changes in headspace gas volume in sewers. These changes cause sewer air to be forced out of the collection system through manholes or other openings. At lower flow rates and volumes, the headspace volume in sewers is greater than at higher flow rates and volumes. The loss of air from the sewers by changes in liquid levels is analogous to the breathing losses that occur when storage tanks are filled.

A thermal differential resulting from differences in the temperature of sewage and the headspace air can cause air flow to be induced. These differentials can occur due to diurnal or seasonal changes in the ambient air and sewage temperatures. The buoyancy due to the property of warm air rising and cold air falling governs the air movement or ventilation in sewers, which, in turn, influences VOC losses. The discharge of warm wastewater or steam and blowdowns from boilers can warm up the sewer temperatures locally, thereby causing conditions conducive to creating warm air currents and stripping of VOCs contained in the wastewater.

5.3 PRELIMINARY/PRIMARY TREATMENT

As discussed above, several POTW unit processes can be grouped based on emissions mechanisms and operational characteristics. Preliminary/primary treatment at most POTWs comprises some or all of the following unit processes:

- Headworks (includes influent sewers, pumping, screening, comminution)
- Grit removal
- Channels
- Primary sedimentation flow equalization

5.3.1 Process Description for Preliminary/Primary Treatment

The preliminary treatment processes at POTWs include ventilated and nonventilated headworks, aerated and non-aerated grit removal, open channel flow meters and sewage receiving facilities. Some plants include the capability of accepting sewage from sewage pumping trucks. Sewage is often added by gravity flow at or near the headworks. Raw sewage arriving at POTWs generally passes through a headworks process in which it is screened or comminuted to remove or grind up large materials such as rags, sticks and other coarse debris. After screening, grit, which consists primarily of heavy inorganic particles such as sand and silt, is removed either by aerated grit tanks or by a non-aerated settling process. Aerated grit chambers work by imparting a helical flow pattern to the sewage by aerating one side of the chamber. The solids from grit removal are generally disposed of off site in a landfill. Aeration allows the heavier grit particles to settle while keeping the lighter organic material in suspension. Emissions are due to the stripping action of aeration in the grit chamber. Emissions from non-aerated grit chambers are usually lower than from aerated grit chambers and are due to volatilization from the surface, which is under relatively quiescent conditions.

The primary sedimentation processes at POTWs include sedimentation or settling tanks that are either covered or uncovered and, in some facilities, primary skimmings or scum concentrators and primary sludge thickeners. The main function of primary sedimentation tanks is to remove readily settleable solids. Floating material (known as scum or skimmings), when present, is also removed, although not by sedimentation. Thus, wastewater suspended solids are removed from primary settling tanks on subsequent units, thereby reducing organic loadings before further treatment. Primary sedimentation tanks can be either rectangular or circular and include scrapers for collecting settled sludge from the bottom of the tanks. In some facilities, sludge is collected in a sump and pumped to a thickening process to concentrate the solids before further processing. Light greases and oils or scum float on top of the tanks and are typically collected in a sump before being pumped to a concentration process.

Flow equalization tanks or ponds are sometimes used to store primary effluent for short periods of time to dampen flow rate variations and optimize downstream treatment process variations. Low-capacity surface aerators are often used on equalization tanks to prevent the wastewater from becoming septic.

5.3.2 Emission Mechanisms for Preliminary/Primary Treatment

Emissions during preliminary treatment can be generated through various mechanisms, depending on the types of processes used. Headworks, non-aerated grit removal, sewage dumping and inlet channel flow meters will generate emissions from volatilization from quiescent and turbulent water surfaces. In addition, emissions can occur due to the turbulence created as wastewater falls over weirs and from the surface area of the wastewater at the weir. Aerated grit chamber emissions can originate from mass transfer from the water surface and from the stripping action of the rising bubbles used for aeration. VOCs in the wastewater are transferred from the wastewater to the aeration bubbles across the bubbles gas–liquid interface. The bubbles escape to the atmosphere, enabling the stripping of VOCs transferred to the air bubble.

VOC emissions from primary sedimentation and primary sludge thickeners are dominated by two mechanisms: volatilization from quiescent surfaces and stripping due to the fall of primary effluents from weir drops. Previous efforts at quantifying emissions from POTWs have indicated that, for volatile species, quiescent surfaces may account for only 10 to 30% of the emissions from primary sedimentation tanks, whereas stripping of VOCs caused by weir drops may account for the remainder of the emissions.[8]

Quiescent surface volatilization and surface aerator turbulence are the mechanisms contributing to VOC emissions from flow equalization tanks. Because of the high amount of turbulence created by surface aerators, VOC emissions from unit processes using surface aeration could be significant and would be large compared with those from units having a quiescent surface. However, if the surface area of the tanks is large and the detention time is high, then the VOC emissions from such tanks could be significant.

5.3.3 Key Factors Affecting Emissions from Preliminary/Primary Treatment

The factors that affect VOC emissions from preliminary/primary treatment processes are:

- **Vapor pressure:** VOCs having a higher vapor pressure (high Henry's constant) volatilize more than those VOCs with a lower vapor pressure (low Henry's constant).
- **Weir configuration:** The higher the drop between water surfaces, the higher the emissions. Longer weirs and shallow tailwater depths also result in higher emission rates.
- **Surface area:** As would be expected, all conditions being equal, VOC emissions from wastewater will be higher from unit processes having a higher surface area than from unit processes with lower surface areas.
- **Gas to liquid ratio:** The higher the ratio of air to wastewater flow, the higher the VOC emissions. The emission rate is highly sensitive to the gas-to-liquid ratio.
- **Covers/ventilation:** In covered unit processes, emissions will be suppressed and a higher proportion of VOCs will remain in solution in the wastewater than in units that are not covered. Ventilation of a covered headspace will decrease the concentration of the VOCs in the headspace, causing VOCs to be driven from the wastewater to the headspace due to the higher concentration gradient between the liquid and the headspace.
- **Other variables:** All other conditions being equal, higher detention times and higher temperatures will generally result in higher emissions.

5.4 BIOLOGICAL TREATMENT

In aerobic biological treatment, microorganisms use oxygen to metabolize and remove organic substances that exert an oxygen demand. Organics in the wastewater that are readily available as food to microorganisms serve as a carbon and energy source for microbial cell tissue at the expense of the energy produced from the metabolism of the organisms. In aerobic systems, the end products of these metabolic reactions are carbon dioxide, water and newly synthesized microorganisms. Two types of aerobic biological treatment processes are generally used — suspended growth (activated sludge) and attached growth (trickling filters and rotating biological contactors). These treatment processes are aerobic, meaning oxygen is added to the system through aeration diffusers, mechanical aeration systems and natural ventilation.

5.4.1 PROCESS DESCRIPTION OF BIOLOGICAL TREATMENT

Activated sludge is the most common biological treatment process used at many POTWs. Activated sludge is a suspension of flocs of microorganisms, both active and dead, in a solution that contains entrapped and suspended colloidal and dissolved organic and inorganic materials. The basic unit used for activated sludge is an aeration basin (or series of basins) in which a suspended biomass or mixed liquor is allowed to use soluble organic matter contained in the effluents from primary settling tanks. The activated sludge process has a number of design variations. The level of VOC emissions from aeration basins depends on the type of aeration system used to supply oxygen to the system. The types of systems used include mechanical aeration, diffused air and high purity oxygen (HPO).

The second major type of biological treatment involves attached growth media systems that provide solid surfaces on which grows a microbial layer (slime) that is exposed to wastewater and air. Under aerobic conditions, the organic matter available in the wastewater is used as food by the organisms contained in the slime layer. The air supplied from the ambient environment and the ventilation of air caused by the differences in the temperature of the wastewater and the media of the unit process provide the needed aerobic environment.

The diffused air activated sludge process requires large volumes of air diffused through the liquid stream to achieve dissolution of the oxygen into the liquid. The aerobic biomass requires adequate oxygen, i.e., more than the oxygen demand exerted to maintain optimum biodegradation activity. Many facilities use fine bubble diffusers to increase oxygen transfer efficiency. Fine bubble diffusers can be designed with either grids of diffuser plates or domes on the floor of the aeration tank. Other facilities use systems known as coarse bubble diffusers that produce larger bubbles. More air volume is required for coarse bubble diffusers because the system is less efficient due to the lower bubble surface-to-air volume ratio.

The HPO activated sludge system operates under the same basic principle as the diffused air system, except that pure oxygen is used rather than atmospheric air. The main advantages of HPO are the decreased energy required for dissolving oxygen and improved biokinetics. Oxygen is usually generated onsite cryogenically by low-temperature distillation. The aeration tanks are covered and the HPO is injected into the headspace between the liquid and the tank cover. Mixers along the length of the process are used to entrain HPO into the liquid stream. Unlike aeration systems using air, which contains nitrogen, HPO systems do not contain nitrogen in the feed stream, hence, the volume of pure oxygen required is considerably less than the air required. Therefore, the venting rate in HPO systems is greatly reduced and is controlled by the oxygen concentration in the headspace and the activated sludge mixed liquor. The venting rate is much lower in HPO systems than in diffused air systems.[9,10]

In biological treatment processes using mechanical aeration, oxygen transfers from ambient air into the wastewater and is achieved by the mechanical agitation of the liquid stream. The process generally involves the use of turbines, brushes or blades mounted throughout the aeration tank. The aerators cause high turbulence near the aerators with decreasing levels of surface turbulence as liquid moves away from the aerators.[11]

Attached growth media processes rely on the contact of wastewater with biomass developed on fixed media such as rocks and plastic media. The most commonly used attached media growth process is the trickling filter. Generally, effluent from the primary sedimentation tanks is sprayed onto the trickling filter by a rotary distributor. As wastewater trickles through the filter medium, microorganisms metabolize organic constituents and remove them from the wastewater. The resulting treated wastewater collects in an underdrain before it is routed to a secondary clarifier. Air vents are placed near the bottom of the filter to allow air to be drawn down or pushed up through the filter, depending on ambient air conditions. Other attached growth treatment systems include rotating biological contactors (RBCs), biological tower systems, etc.

5.4.2 Emission Mechanisms for Biological Treatment

Emission mechanisms for a biological treatment process include surface volatilization and transfer of VOCs from the wastewater to the rising air bubbles used for aeration. In addition, VOCs can be emitted due to aerosol particles primarily from mechanical aeration and from emissions associated with weir drops due to stripping. Other mechanisms are also responsible for the removal of VOCs from wastewater, thereby significantly reducing their emissions. These competing mechanisms include biodegradation and solids adsorption. VOCs that are highly biodegradable can have significantly lower air emission rates than those that are not readily biodegraded.

Emissions from trickling filters occur as a result of two processes: the splash of wastewater as it impacts the filter media and the trickling of wastewater through the media. The splashing effect is highly turbulent and can cause the release of significant amounts of VOCs. The trickling effect increases the surface area of the wastewater exposed to air, thereby increasing mass transfer of VOCs from wastewater to air and increasing the air emissions. Emissions from RBC systems are also governed by the various mechanisms mentioned above.

5.4.3 Key Factors Affecting Emissions for Biological Treatment

The key factors that affect emissions for activated sludge systems are:

- **Gas to liquid ratio:** For diffused air systems, a higher ratio of airflow-to-wastewater flow will significantly increase emissions. Because HPO has a low gas-to-liquid ratio, emissions from a HPO system are significantly lower compared to mechanical and diffused aeration systems. Fine bubble aeration has a lower gas-to-liquid ratio than coarse bubble aeration due to better mass transfer. Therefore, treatment systems using fine bubble aeration have lower VOC emissions than coarse bubble aeration systems.[11,12]

- **Biodegradation rate:** The higher the VOC biodegradation rate, the lower the emissions are. Compounds that are highly biodegradable will be degraded before they have an opportunity to be emitted in significant amounts. Biodegradation rates of VOCs may differ from POTW to POTW because of the degree of adaptation of microorganisms to the VOCs.[9]
- **Aerator characteristics:** For mechanical aeration systems, the rotational characteristics, size and power of the aerators will affect emissions.
- **Other factors:** Other factors that affect emissions are temperature of the wastewater, detention time, basin surface area, diffuser type and other system design parameters.

The factors that impact emissions from trickling filters and RBCs are:

- **Media surface area:** Larger surface areas result in higher mass transfer rates and higher emissions than in systems with lower surface areas.
- **Ventilation rate:** Increased ventilation rates will promote higher mass transfer rates and hence higher VOC emission rates. In most trickling filters, ventilation is created naturally by the differences in temperature of the wastewater and the air. The ventilation rate can be estimated by measurement of the liquid temperature, air temperature, liquid loading rate per unit surface area, the type of medium and the filter dimensions. RBC ventilation is not as significant as in trickling filters.[10]

5.5 POST-BIOLOGICAL TREATMENT

Treatment processes downstream of biological treatment can be divided into the following unit processes for the purposes of emission characterization:

- Secondary clarification
- Tertiary filtration
- Disinfection using chlorination

5.5.1 Process Description for Post-Biological Treatment

Secondary clarification is a process in which the suspended solids of the mixed liquor from the aeration tanks of an activated sludge system are allowed to settle under gravity within the detention time of the secondary sedimentation tanks. The mixed liquor from the aeration tanks is introduced to a clarifier or sedimentation tank in a manner that evenly distributes the flow across the settling area. The solids in the mixed liquor settle to the bottom of the clarifier and are moved to a hopper at the bottom of the clarifier by a series of scrapers. A portion of the solids settled is returned to the activated sludge system and the remainder is then pumped to the downstream solids processing system. The secondary clarifiers have two sources of emissions — the quiescent clarifier surface and the weir drops. The VOCs adsorbed onto the settled solids may also be biodegraded to some extent.

Secondary clarification in the case of attached growth systems such as trickling filters and RBCs is carried out in secondary settling tanks. Unlike the activated sludge process, solids settled in the clarifier are not basically returned to the headend of these processes. Optional recirculation of the effluent is practiced in certain cases to maintain the hydraulic flow rate of the system and to maintain active biofilms on the media.

Tertiary or effluent filters are used downstream of secondary clarifiers and typically use a granular medium to filter the solids from the secondary effluent that did not settle in the clarifiers. The filters may be open (gravity) or enclosed (pressure) filters. Gravity filters have quiescent operational characteristics that typically result in insignificant emission levels. However, in most cases, by the time the wastewater reaches the tertiary filters, almost all of the VOCs have been removed in upstream processes, leaving only low levels of VOCs to be emitted from the filters. Pressure filters are totally enclosed and therefore little or no emissions occur during filtration. Filters are typically cleaned by having air or water forced through them, usually in the opposite direction of the filtering process. Because of the short duration of this back washing (typically 10 minutes or less per day), emissions are expected to be a small fraction of those from the overall filtering process.

Disinfection is used commonly in wastewater treatment processes to destroy indicator and disease-causing organisms. The most common method of disinfection in wastewater treatment is chlorination using chlorine in the form of chlorine gas, calcium hypochlorite or sodium hypochlorite. Chlorine is diffused into the effluent and the mixture is allowed to flow through tanks or channels that are used to provide time for the chlorine to contact and react with the effluent to achieve adequate disinfection. The ideal flow pattern for chlorine contact is plug flow, which is typically obtained using a serpentine flow pattern by constructing interior baffle walls within a rectangular tank. Although the tanks can be either covered or uncovered, they are typically uncovered because of the low levels of odors that originate from the disinfection process.

5.5.2 EMISSION MECHANISMS FOR POST-BIOLOGICAL TREATMENT

Emissions from secondary clarifiers are caused by two mechanisms — mass transfer from the clarifier's quiescent surfaces and turbulence at the weir drops. Previous efforts at quantification of VOCs from POTWs have indicated that the clarifier surface may account for only 10 to 30% of emissions from secondary clarifiers, whereas weir drops can account for the remaining emissions.[10] Emissions from chlorine disinfection processes or from scrubber systems using hypochlorite for odor control will occur from the surface of the contact basins and any weirs or the scrubbers used in the process. However, the surface area of the chlorine contact tanks is relatively small. Emissions of chlorine from the disinfection process are relatively low in most cases because the chlorine reacts rapidly with the wastewater. However, chlorine can react with organics contained in the effluent to form trihalomethanes (THMs) such as chloroform and bromoform. A chlorine disinfection system is unique in that VOCs may be formed in the process rather than originate from the influent to the system, resulting in an increase in HAP liquid phase concentrations. The VOCs that are formed have an opportunity to volatilize from the surface of a chlorine contact basin or from the vent of a scrubber system and points of turbulence such as weirs or effluent outfalls.

Tertiary filtration of wastewater requires a large filter surface area to effectively filter the effluent. Although this surface is large, it is quiescent, with little turbulence; therefore, the VOC emissions are relatively low. Weir drops can be present at the end of processes to regulate process detention times and flows. The elevation of the body of water that receives the final effluent may be significantly lower than the surface of the filters. If this is the case, a large amount of turbulence could be created at the large drop between the outlet of the filter and the water surfaces. This turbulence could result in significant emissions. However, as discussed previously, by the time the wastewater reaches the tertiary filters, usually almost all of the VOCs have been removed in upstream processes, leaving only low levels of VOCs to be emitted from the filters. On the other hand, if low emission upstream processes such as HPO are utilized, emissions from a large drop at tertiary filters could be significant in terms of relative proportions, but not necessarily in terms of total mass emitted. Also, THMs formed during chlorine disinfection could be emitted from tertiary treatment filters.

5.5.3 Key Factors Affecting Emissions for Post-Biological Treatment

The key factors affecting emissions from post-biological treatment units are surface area, weir configuration (height of the weir drop, type of weir and weir length), flow rate and tank dimensions. Typically, a large weir drop will be the only significant cause of emissions. If certain organics are present in the effluent, THMs formed during chlorination will be emitted at weirs and weir drops. The chlorine (Cl_2) injected in the effluent combines with water to form hypochlorous acid (HOC1) and hydrochloric acid (HCl). Cl_2, HOC1 and the hypochlorite ion (OCl^-), disassociated from HOCl, are strong oxidizing agents and react with any reducing compounds present in wastewater. When such oxidative reactions are complete, the remaining active chlorine species react with ammonia or organic nitrogen compounds to form chloramines. Chlorinated organic compounds can also be formed. The nature and concentration of the reactive species will determine the formation and yield of chlorinated organic compounds, including the following THMs: chloroform, dibromochloromethane, dichlorobromomethane and bromoform. Humic and fulvic acids are generally the most common THM precursors present in wastewater and therefore contribute the greatest to the formation of THMs. Full scale and laboratory testing showed that if ammonia or organic nitrogen compounds are not present to react with the chlorine compounds, larger quantities of THMs could be formed. Wastewater treatment systems that nitrify therefore have a potential to form larger amounts of THMs than systems that do not nitrify.

A full-scale study was done at the Green Bay Metropolitan Sewerage District (GBMSD) to quantify the formation and emissions of VOCs, specifically THMs from the chlorine disinfection process. An empirical model was developed to represent the chlorination disinfection system at the GBMSD, as it relates to THM formation:[13]

$$C_{THMs} = a + b[\log T_C]\ C_D$$

C_{THMs} = Total trihalomethanes in the GBMSD plant effluent at the end of the chlorination process (ppb)
T_C = Contact time (min)
C_D = Chlorine dosage; residual chlorine in the contact basin
A = intercept
B = slope

The model is calibrated under the assumptions of nitrification conditions, neutral pH, stable temperature and organic carbon concentrations as follows:

$$C_{THMs} = 40.3 + 4.64[\log T_C]\ C_D$$

A similar model may be applicable at other treatment plant disinfection units, but different coefficients may apply.

5.6 SOLIDS HANDLING

For the purposes of emission characterization, the processes that treat the solids removed from biological processes can be divided into the following categories:

- **Enclosed Solids Handling Processes:** These include digestion, gravity thickening, belt press, centrifuge dewatering, composting conveyance, heat drying, pelletization and storage.
- **Open Solids Handling:** These include sludge drying beds, lagoons, composting conveyance, storage and truck loading facilities.
- **Dissolved Air Flotation (DAF) Thickening**.

These categories allow a simplified understanding and analysis of the emissions from solids handling processes. Enclosed solids handling processes are generally placed within a building and can therefore be controlled by collecting and treating the building ventilation air. Open solids handling processes are not enclosed and therefore require alternate methods of emissions control. DAF thickening units can be covered or uncovered.

5.6.1 PROCESS DESCRIPTION FOR SOLIDS HANDLING

Sludge digesters can be either aerobic or anaerobic biological processes. In both cases, microorganisms treat sludge by:

- Decomposing and stabilizing organics
- Reducing the sludge mass and volume
- Destroying pathogens

The anaerobic digestion of sludge is carried out in tanks (digesters) in the absence of oxygen. These tanks have either fixed or floating covers. The anaerobic process produces a by-product gas that consists primarily of methane and carbon dioxide. The aerobic digestion of sludge is also carried out in tanks, but in the presence of oxygen, and these tanks may be open to the atmosphere or enclosed. The aerobic digestion process produces a gas that is primarily carbon dioxide.

Sludge thickening and dewatering are physical processes used to decrease the liquid content of the sludge. A typical thickening process increases the solids content of the sludge from 3 to 10%. Dewatering increases the solids content of thickened sludge up to 40% solids. Thickening processes include gravity thickening clarifiers, DAFs, centrifuges and gravity belts. Dewatering processes include belt presses, filter presses and centrifuges.

The gravity thickening process is similar to primary or secondary sedimentation and occurs in circular or rectangular tanks. Heavier particles settle to the bottom of the tanks and the weight of the blanket forms compresses and thickens the solids further. Lighter greases and oils that collect on the tank surface are skimmed off and the effluent is discharged over a weir. In the DAF process, solids are pressurized with air. When the pressurized liquid is released to atmospheric pressure, microbubbles escape. These microbubbles give the sludge particles buoyancy and carry them to the surface to form a concentrated sludge blanket at the top of the DAF unit that is then skimmed off. Belt presses remove moisture from the sludge by compressing it between two fabric belts squeezed between a series of rollers. The resulting dewatered cake is collected on conveyor belts for disposal or further processing. The centrifuge process uses a bowl rotating at high speeds to separate solids and liquids. Because of the differences in density, the centrifugal force separates the liquid or centrate from the solids. The dewatered solids collect on the outer sides of the bowl and are removed for disposal or further processing.

Other solids handling operations include conveyor belts, storage hoppers and truck loading. After dewatering, cake solids are often conveyed to storage before the cake is hauled off site for disposal. Some facilities load trucks directly from the dewatering process without intermediate storage.

Sludge drying operations include static drying beds and mixed drying beds. Sludge drying in drying beds is a process of simple moisture evaporation from the solids. Static beds are left undisturbed and open to air. The drying rate depends on temperature, relative humidity and exposed surface area. In mixed beds, the sludge is periodically turned over to expose more sludge surface area to air, resulting in a product usually in the range of about 20 to 40% moisture. VOCs present in the sludge can be emitted to the atmosphere during the drying process. In heat drying operations, sludge solids are heated either directly or indirectly in an enclosed system. Dry pellets with less than 5% moisture are generally produced. VOC emissions from drying operations are usually low because of their depletion in the upstream sludge processing operations. Any odors and VOCs emitted from these operations are collected and treated through thermal oxidizers at high temperatures of about 1200 to 1400°F. When these units are properly operated, VOC and odor emissions are usually very negligible

VOC emissions from incinerators, which are usually followed by secondary combination units to control air pollution, are generally low. Because the POTW sludge incinerators are determined by EPA to be insignificant sources of VOC emissions, they were delisted from the major sources of emissions and there is no requirement for MACT.

5.6.2 EMISSION MECHANISMS FOR SOLIDS HANDLING PROCESSES

VOC emissions from aerobic sludge digesters are primarily due to the stripping action of the air added to the process. Emissions from anaerobic systems are associated with leaks in the system — from covers, valve stems and other sources such as annular space between the digester and its outside wall. Gas produced in the process is used in combustion sources such as flares, internal combustion engines and boilers. These sources, discussed in Section 5.7, emit pollutants that are the products of combustion.

Emission mechanisms for other solids handling processes are shown in Table 5.1.

TABLE 5.1
Emission Mechanisms for Solids Handling

Process	Emission Mechanisms
Belt Press Dewatering/Gravity Belt Thickening	Volatilization from biosolids surface
Gravity Thickening	Stripping at weirs/surface volatilization
DAFs	Stripping action of air bubbles
Aerobic Digestion	Stripping of VOCs remaining after biodegradation
Anaerobic Digestion	Volatilization from surface and stripping of VOCs remaining after biodegradation due to digester-gas evolution
Drying Beds	Volatilization from biosolids surface, mixing action
Heat Drying and Incinerator Systems	Volatilization from biosolids at high temperatures
Conveyors/Truck Loadout/Storage	Volatilization from biosolids surface

5.6.3 KEY FACTORS AFFECTING EMISSIONS FOR SOLIDS HANDLING

In general, VOC emissions from solids handling processes including digestion are relatively low and insignificant in comparison with the emissions from aerated grit chambers and activated sludge aeration basins. Many of the VOCs present in the raw wastewater have been either removed or degraded in the upstream physical and biological processes. Adsorption of VOCs to solids is a relatively minor removal mechanism. The factors that affect emissions from solids handling processes are shown in Table 5.2.

5.7 COMBUSTION PROCESSES

A number of processes commonly used at POTWs combust fuels. The pollutants emitted from these processes are a product of the combustion process and are therefore different from the VOCs emitted from the other POTW liquid and solids processes.[14,15] The pollutants emitted from combustion processes typically include the following:

- VOCs
- Oxides of nitrogen (NO_x)
- Carbon monoxide (CO)
- Hydrocarbons
- Oxides of sulfur (SO_x)
- Particulate matter (PM)
- Products of incomplete combustion (PICs)

5.7.1 PROCESS DESCRIPTION FOR COMBUSTION PROCESSES

As reported by Caballero and Griffith,[16] four types of combustion processes are commonly found at POTWs.

TABLE 5.2
Key Factors Affecting Emissions from Solids Handling

Process	Factors Affecting Emission
Belt Press Dewatering/Gravity Belt Thickening	Solids flow rate, solids surface area, ventilation rate (if enclosed)
Gravity Thickening	Surface area, weir configuration, detention time
DAFs	Gas-to-liquid ratio, surface area
Aerobic Digestion	Gas-to-liquid ratio, surface area, degree of mixing or turnover rate
Anaerobic Digestion	Surface area, degree of mixing
Drying Beds	Surface area, amount of mixing or turnover rate
Heat Drying and Incineration	Temperature, mixing or turnover rate
Conveyors/Truck Loadout/Storage	Surface area, ventilation rate (if enclosed)

5.7.1.1 Internal Combustion Engines

These typically are used to produce electricity where excess digester gas is available to burn as a fuel for the engines. Digester gas contains about 60 to 65% methane and has a similar percent of the energy value as methane (natural gas). The engines are used either to generate power utilized in the plant or to directly drive equipment such as large air compressors or pumps. The engines are usually designed to burn both digester gas and natural gas or a mixture of both. Some engines are designed to be "lean burning," meaning they operate with a high air-to-fuel ratio to reduce emissions. Lean burning engines typically use a prechamber to ignite a lean burning main combustion chamber.

5.7.1.2 Flares

If a POTW produces more digester gas than can be used in boilers or for power generation, etc., it is burned in flares. Flares are required to reduce odors, avoid an explosion or fire hazard and destroy VOCs. Flares are typically designed to ignite the digester gas by passing it through a "curtain of flame" developed by a ring-type natural gas pilot flame. The digester gas is deflected across the pilot flame by a baffle. Some flares are designed to be highly efficient in destroying the VOCs by providing a large combustion chamber that increases detention time. Much of the organic emissions from flares is unburned methane; methane is typically not a regulated pollutant in the United States.

5.7.1.3 Boilers

Boilers combust fuels to heat water to produce either steam or hot water. This energy is used primarily for heating building(s) or digester biosolids. Boilers can be designed to burn digester gas, natural gas and fuel oil.

5.7.1.4 Incinerators

The incineration process combusts or burns biosolids in the presence of oxygen supplied by air. The biosolids are used as a fuel in incinerators. The combustible materials in biosolids comprise grease (fats), carbohydrates and proteins. Carbon, hydrogen and sulfur are chemically combined in proteins, whereas carbon and hydrogen are chemically combined in carbohydrates and fats. If the fuel content of the biosolids is high enough, the biosolids can be burned "autogenously" without supplemental fuel. However, supplemental fuel is usually required and natural gas or fuel oil is typically used. The two common types of biosolid incinerators are the multiple hearth and the fluidized bed. The multiple hearth incinerator is a cylindrical refractory-lined steel shell containing a series of horizontal refractory hearths located one above the other. An incinerator typically has three zones: the drying, burning and cooling zones. A fluidized bed incinerator operates by setting the biosolids and a sand bed in fluid motion by passing combustion air through the fluid bed zone in a homogenous boiling motion. The oxygen in the air quickly reacts to combust the solids because the solids to be burned are surrounded by air. Exhaust gases from the incinerators are vented to air pollution control devices. Some type of control device, usually a wet scrubber, is used to control particulates, and thermal oxidation is often used to control hydrocarbon emissions.

5.7.2 EMISSION MECHANISMS FOR COMBUSTION PROCESSES

The following sections summarize the mechanisms for emissions of combustion products.

5.7.2.1 VOCs

VOCs associated with the biosolids subjected to combustion are not high in concentration because most of the VOCs are removed in upstream processes. However, any VOCs still present will be destroyed at the high temperatures prevailing in the combustion devices and the devices that follow to control air pollution, such as afterburners and thermal oxidizers. When such devices are not used, some VOC emissions may occur. However, in combustion systems, usually afterburning and thermal oxidation are practiced in conjunction with the combustion system. Hence, VOC emissions are generally within the limits of state and federal air quality regulations.

Interestingly, however, in internal combustion engines, the formation of large quantities of formaldehyde has been recently reported (Kwang et al.[17]).

5.7.2.2 Oxides of Nitrogen

Oxides of nitrogen, primarily NO (nitric oxide) and NO_2 (nitrogen dioxide), are formed by either or both of two mechanisms — thermal NO_x or fuel NO_x. Thermal NO_x is formed by reactions between nitrogen and oxygen in the air used for combustion. Fuel NO_x results from combustion of fuels such as biosolids or heavy oils that contain organic nitrogen.

5.7.2.3 Carbon Monoxide

Carbon monoxide results from the incomplete combustion of carbonaceous fuels such as natural gas and digester gas.

5.7.2.4 Hydrocarbons

Hydrocarbon emissions are caused by incomplete combustion of organics in fuels. For incineration, hydrocarbons can also originate from volatile organics that may be present in the biosolids.

5.7.2.5 Oxides of Sulfur

SO_x are formed when sulfur compounds found in fuels are oxidized in the combustion process. Digester gas usually contains sulfides in the form of hydrogen sulfide and is sometimes treated to remove sulfides. Fuel oil and biosolids also both contain sulfur.

5.7.2.6 Particulates and Metals

Particulates and metals can originate from the material being combusted, such as biosolids. For a multiple hearth incinerator, 15 to 30% of the ash content of the filter cake will become airborne in the incinerator exhaust. Emission control equipment can remove most of this. Small amounts of particulates also come from noncombustible ash that may be present in the fuel being burned. Particulate emissions from other combustion processes are usually low because of the low amount of ash present in the fuel.

5.7.3 PRODUCTS OF INCOMPLETE COMBUSTION

The PICs are formed when oxygen is used in less than the required amounts during the combustion process.[17] Also, they are formed when the temperatures used in the combustion device are lower than the temperatures at which the complete combustion of a given VOC occurs. Hence, it is important to maintain optimal temperatures and oxygen levels in a combustion device to achieve the complete combustion of a specific VOC.

The various types of combustion devices used for the control of VOCs are presented and discussed in Chapter 15 on Control Technology.

5.7.4 KEY FACTORS AFFECTING EMISSIONS FOR COMBUSTION PROCESSES

Factors that affect emissions from combustion processes are summarized in Tables 5.3 through 5.6.

5.8 ESTIMATING EMISSIONS FROM POTWs

Estimating VOC emissions from POTW unit process systems by direct measurements is complex, difficult and costly. Due to these difficulties, most emission estimate determinations are made through the use of emission factors and models.

General fate models are convenient tools to predict the emission rates of VOCs without undertaking elaborate and expensive sampling and analysis of direct emissions from POTW unit processes. The wide range of emission estimate methods is discussed in Chapter 13. However, to provide some context for the emission information presented in Chapters 6 through 11, this subsection identifies the three most widely used fate models: WATER8/WATER9, Toxic Chemical Modeling Program for Water Pollution Control Plants, (TOXCHEM/TOXCHEM+) and the Bay Area Sewage Toxics Emission (BASTE), Model. These models are summarized in Table 5.7.

These models are the “current generation” of general fate models developed in the late 1970s and early 1980s. The “first generation” models were usually programmed as spreadsheets and were updated into newer versions mostly for aeration basins and very few other unit processes. The newer models have the ability to model many of the common unit processes present at POTWs and have been extensively used in studies or regulatory programs by various large POTWs for estimating VOC emissions.

TABLE 5.3
Factors Affecting Emissions from Internal Combustion Engines

Pollutant	Factors Affecting Emissions
NO_x	Air-to-fuel ratio impacts emissions significantly. Rich fuel mix (low air to fuel) decreases NO_X due to lack of oxygen and lower combustion temperature. NO_X reaches peak at slightly lean mix when oxygen is abundant and temperature is high. At increasingly lean ratio, temperature falls along with NO_X emissions. NO_X is significantly lower for digester gas because the high CO_2 gas concentration cools the peak combustion temperature, reducing NO_X.
CO	Low air to fuel ratio causes significant increase in CO because of lack of sufficient oxygen to complete combustion.
Oxides of sulfur	As hydrogen sulfide concentration in the digester gas used as a fuel increases, SO_x emissions will increase proportionately. Processes are available to remove the hydrogen sulfide in the digester gas before combustion. Complete combustion of digester gas will also increase SO_x emissions.
Hydrocarbons	Hydrocarbon emissions are higher when there is more fuel than is required stoichiometrically because of the lack of oxygen for complete combustion. Hydrocarbon emissions are also slightly higher at very high air-to-fuel ratios because of the decreased combustion temperatures.
Particulate matter (PM)	PM levels from natural or digester gas combustion are generally insignificant.

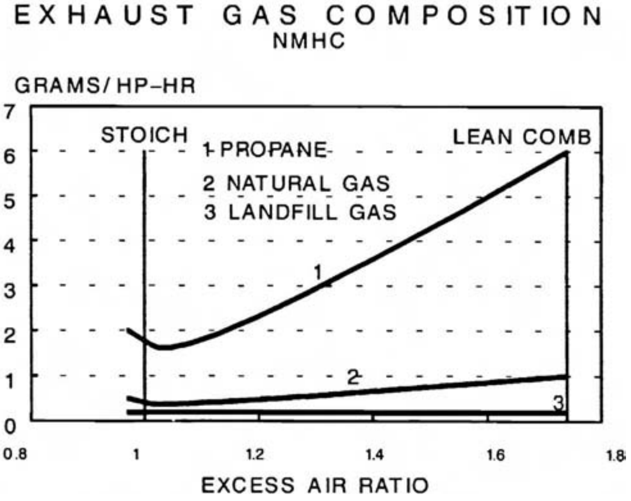


FIGURE 5.1 NO_x and CO emissions from I.C. Engines.

TABLE 5.4
Factors Affecting Emissions from Boilers

Pollutant	Factors Affecting Emissions
NO_x	Peak NO_x occurs at about stoichiometrically equal or zero excess oxygen. NO_x decreases as fuel-to-air mix is lean or rich. Flue gas recirculation decreases NO_X. Increase in temperature significantly increases NO_x. Increase in detention time increases NO_x.
CO	Low air-to-fuel ratio causes increase in CO because of lack of sufficient oxygen to complete combustion. CO will initially increase with increasing detention time, peak and then decrease.
Oxides of sulfur	Higher levels of hydrogen sulfide in digester gas used as a fuel will increase SO_x emissions. Processes are available to remove sulfides in the digester gas before combustion.
Hydrocarbons	Hydrocarbon emissions are higher when there is more fuel than is required stoichiometrically because of the lack of oxygen for complete combustion. Higher temperatures, longer detention time and good combustion air mixing result in lower hydrocarbon emissions.
PM	PM levels from natural or digester gas are generally insignificant.

TABLE 5.5
Factors Affecting Emissions from Flares

Pollutant	Factors Affecting Emissions
NO_x	Peak NO_x occurs at about stoichiometrically equal or zero excess oxygen. NO_x decreases as fuel-to-air mix is lean or rich. Flue gas recirculation decreases NO_X. Increase in temperature significantly increases NO_x. Increase in detention time increases NO_x so enclosed flares could theoretically increase NO_X.
CO	Low air-to-fuel ratio causes increase in CO because of lack of sufficient oxygen to complete combustion. CO will initially increase with increasing detention time, peak and then decrease.
Oxides of sulfur	Higher levels of hydrogen sulfide in digester gas used as a fuel will increase SO_x emissions. Processes are available to remove sulfides in the digester gas before combustion.
Hydrocarbons	Hydrocarbon emissions are higher when there is more fuel than is required stoichiometrically because of the lack of oxygen for complete combustion. Higher temperatures, longer detention time and good combustion air mixing result in lower hydrocarbon emissions. Some flares are designed for significantly lower emissions by providing better mixing and large combustion chamber rather than simply igniting the gas as is done in an "open" type flare design.
PM	PM levels are generally insignificant for a flare that is operating properly.

TABLE 5.6
Factors Affecting Emissions from Biosolids Incineration

Pollutant	Factors Affecting Emissions
NO_x	Rich fuel mix can increase fuel NO_x. At 1800°F, the formation of NO_x is 50% greater than at 1700°F. Fluidized beds operate at low temperatures and low excess air so NO_x is minimized. High filter cake nitrogen will combine with oxygen to form NO_x.
CO	Low air-to-fuel ratio causes an increase in CO because of lack of sufficient oxygen to complete combustion. Low combustion temperature increases CO levels. Good mixing and adequate detention time decreases CO. Conditions that promote low CO can increase NO_x.
Oxides of sulfur	Higher biosolids sulfur content results in higher SO_x emissions. Sulfur in the oxidized sulfate form will not be oxidized. Cake sulfur content can vary widely. SO_2 can combine with water in the scrubber or the atmosphere to form sulfurous or sulfuric acid.
Hydrocarbons	Hydrocarbons are emitted from vaporization of organic biosolids compounds. Hydrocarbon emissions are higher when there is more fuel than is required stoichiometrically because of the lack of oxygen for complete combustion. Higher temperatures, longer detention time and good combustion air mixing result in lower hydrocarbon emissions.
PM and metals	Increased cake ash content will increase the PM that will enter the incinerator exhaust air. The level of PM emitted will depend on the efficiency of the particulate control device. Efficiencies range from 95% for a simple scrubber to 99.9% for a wet electrostatic precipitator. Higher temperatures will volatilize some metals. For multiple hearth, particulates emitted dependent on what hearth solids are burned in.

TABLE 5.7
Overview of Frequently Used Models

Model	Type	Application
WATER8	EPA) Public Domain)	Collection Systems
WATER9	(EPA) Public Domain	Treatment Systems
TOXCHEM	Proprietary	Collection Systems
TOXCHEM+		Treatment Systems
BASTE	Proprietary	Limited at collection systems structures (drop only) Treatment Systems

5.9 SUMMARY

About 16,000 POTWs in the United States collect and treat approximately 114 million cubic meters per day (30 billion gallons per day) of municipal wastewater.

These POTWs and their appurtenances serve as major pathways for the discharge of water. Emissions of VOCs from collection systems and wastewater treatment unit processes are usually made by three widely used general fate models. These are Water 8/Water 9, BASTE and TOXCHEM/TOXCHEM +.

REFERENCES

1. Metcalf and Eddy, Inc., *Wastewater Engineering: Collection and Pumping of Wastewater*, McGraw-Hill Book Company, New York, 1981.
2. Corsi, R.L., Chang, D.Y. and E.D. Schroeder, Assessment of the Effects of Ventilation Rates on VOC Emissions from Sewers, *U.S. EPA/WPCF Workshop and Proceedings, Air Toxic Emissions and POTWs*, Alexandria, Virginia, 1989.
3. Howle, R.H. and Zukor, C.H. *Low Emissions Sewer Systems for Industry*, Project 92-PRE-1, Water Environment Research Foundation, Alexandria, Virginia, 1994.
4. Pescod, M.B. and Price, A.C., Fundamentals of sewer ventilation as applied to the tyneside sewerage scheme, *Water Poll. Contr.* (G.B.), 90(1), 17–33, 1981.
5. Pescod, M.B. and Price, A.C., Major factors in sewer ventilation, *J. Water Poll. Contr. Fed.*, 54: 385, 1982.
6. Thistlethwayte, D.K.B., *The Control of Sulphides in Sewerage Systems*, 1st ed. Ann Arbor Science Publishers, Ann Arbor, Michigan, 1972.
7. Pomeroy, R., The pros and cons of sewer ventilation, *Sewer Works J.*, 17: 203, 1945.
8. Pincince, A.B., Transfer of oxygen and emissions of volatile organic compounds at clarifier weirs, *Water Envir. Res. J.*, 63: 114-119, 1991.
9. Rajagopalan, S.C. et al., Comparison of methods for determining biodegradation kinetics of volatile organic compounds, presented at the Water Environment Federation 67th Annual Conference and Exposition, Chicago, 1994.
10. Bell, J. et al., *Modeling the Stripping and Volatilization of VOCs in Wastewater Collection and Treatment Systems*, Project 91-TFT-1, Water Environment Research Foundation Report, 1998.
11. Card, T.R., Designing wastewater treatment plants to minimize air emissions, presented at the AIChE 1990 Summer National Meeting, 1990.
12. Desing, W.E., Aeration systems selection and specification to minimize toxic air emissions, presented at the 65 Annual Meeting of the Central States Water Pollution Control Association, 1991.
13. Desing, W.E. and Robinson M., Formation and emissions of trihalomethanes from chlorine wastewater disinfection, presented at the 68th Annual Conference of the Water Environment Federation, 1995.
14. Tri TAC, *Guidance Document on Control Technology for VOC Air Emissions from POTWs*, Tri-Tac in collaboration with California POTWs and Air Quality Regulatory Agencies, CH2M HILL, 1994.
15. Waukesha/Dresser, Gas Engine Emissions Technology, Waukesha, Wisconsin, 1993.
16. Caballero, R.C. and Griffith, P., VOC Emissions from POTWs, *U.S. EPA/WPCF Workshop and Proceedings, Air Toxic Emissions and POTWs*, Alexandria, Virginia, 1989.
17. Kwang, W.Z., Sachs, F. and DiSalvo, D.L., Do VOC emissions from WPCPs affect ambient air quality? unpublished report of the New York City Department of Environmental Protection, New York, 1999.

6 VOC Emissions from Sewers

David Olson, Richard Corsi and Prakasam Tata

CONTENTS

6.1 Introduction 97
6.2 Factors Affecting Sewer VOC Emissions 98
6.3 Emission Mechanisms 99
6.4 Theoretical Considerations 100
6.5 Tracer Studies 104
6.6 Field Monitoring 105
6.7 Drop Structures 106
6.8 Air Exchange Rates 107
6.9 Modeling 111
    6.9.1 Screening Techniques 111
    6.9.2 CORAL+ 112
    6.9.3 WATER9 113
    6.9.4 TOXCHEM+ 113
    6.9.5 naUTilus 113
6.10 Summary 113
References 114

6.1 INTRODUCTION

Dischargers to sewers include major industrial facilities, e.g., petroleum refineries and pharmaceutical manufacturers, smaller commercial establishments, (e.g., dry cleaners and graphic arts facilities), public institutions, (e.g., universities) and residential households that use consumer products containing VOCs. Thus, municipal sewers are important with respect to VOCs emissions for two reasons. First, the composition of VOCs and HAPs observed in wastewater provides a qualitative "snapshot" of the potential for emissions from non-mobile sources in urban areas. Second, sewers themselves may serve as important area sources of VOC emissions.

The primary HAPs emitted by POTWs include dimethylbenzene isomers (xylenes), dichloromethane (methylene chloride), toluene, benzene, ethylbenzene, chloroform, tetrachloroethene (perchloroethylene) and naphthalene. Additional

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

HAPs are often observed at lower concentrations, e.g., 1,4-dichlorobenzene, 1,2-dichloroethane, vinyl chloride and methyl-t-butyl ether (MTBE) are now observed at relatively high concentrations in some municipal wastewater. While the concentrations of most of these HAPs and VOCs are typically observed at less than 10 to 20 μg/L in the influent streams of POTWs, the large volumes of wastewater collected and transported by sewers suggest that significant mass discharges and airborne emissions of these compounds may occur from municipal sewers. Furthermore, the VOC concentrations observed in POTW influents may be significantly lower than the actual VOC concentrations in sewers if significant emissions occur from the sewer.

Total mass discharges of VOCs to municipal wastewater collection systems are often estimated based on mass loadings in the influent streams of downstream treatment facilities. Such discharges have historically led to concerns related to (1) accumulation of gases that approach or exceed lower explosion limits (LOELs), (2) detrimental impacts on biological treatment systems and (3) toxic effects on natural waters. A new concern of risk to public health has arisen regarding emissions of HAPs from POTWs.[1] Subsequent attention has been focused on volatile HAP emissions from wastewater treatment plants.[2–9] The extent to which VOCs are emitted prior to reaching a wastewater treatment plant, i.e., from sewers that convey wastewater to the plant, has not been largely studied, particularly for municipal sewers.

Although past studies related to VOC emissions from wastewater have focused on wastewater treatment facilities, there is growing evidence that large fractions of volatile chemicals are emitted from sewers before ever reaching a downstream treatment plant.[10] Thus, estimates of volatile chemical discharges to sewers based on mass loadings at treatment plants may be significantly underestimated. Furthermore, the potential for municipal collection systems to serve as significant area sources of chemical emissions is underscored by the fact that the main component of the collection system, namely sewers, are generally distributed throughout the urban areas, often conveying wastes from industries, commercial establishments and residential areas. The various components of a collection system are presented in Chapter 5. Emissions from sewer reaches and drop structures have been studied to a greater extent by a handful of investigators and their associates, notably by Corsi and Bell's groups, than from the other components of the collection system. The studies conducted on sewer reach and drop structure emissions and the results obtained are the basis for the content of this chapter.

6.2 FACTORS AFFECTING SEWER VOC EMISSIONS

Several factors govern the transfer of VOCs to the ambient air along sewer reaches. These include:

- Kinetic energy due to turbulence
- Mixing associates with turbulence in the flowing wastewater stream
- Magnitude of ventilation and patterns associated with the sewer head spoke
- Physical chemical properties of VOCs
- Wastewater fluid properties[11]

The degree of turbulence and mixing caused in sewers depend on their design, e.g., slope and diameter. Ventilation in the sewer headspace is affected by the number of characteristics of the openings between the sewer and its appurtenances and ambient atmosphere, gradients in barometric pressure, buoyancy-driven gas flows, bulk displacement by changes in wastewater flows and liquid drag imparted on overlying sewer gas. The temperature of wastewater can significantly affect such VOC property as Henry's law coefficient as well as interfacial transfer such as the accumulation of surfactants at the air-wastewater interface.[11]

6.3 EMISSION MECHANISMS

Two processes that govern the extent of chemical emissions from sewers are mass transfer and air exchange. The VOC mass transferred from a liquid to the adjacent headspace air can be released to the ambient atmosphere via an exchange of the gases between the two media, which is known as sewer ventilation. Sewer ventilation occurs at openings such as manholes along the length of the sewers. Several factors influence the rate of mass transfer. These include physical and chemical properties of a VOC, fluid and flow characteristics and interfacial surface area.

Figure 6.1 illustrates emission mechanisms for a sewer reach and drop structure. Mass transfer can occur along sewer reaches, a process enhanced as flow becomes more agitated. Such situations are likely to occur along pipes with steeper slopes and higher flow rates, as well as points of confluence, i.e., junction boxes and drop structures. Mass transfer can occur at several points within drop structures, including the falling film, i.e, the water splashing at the tailwater surface and air entrainment in the tailwater pool.

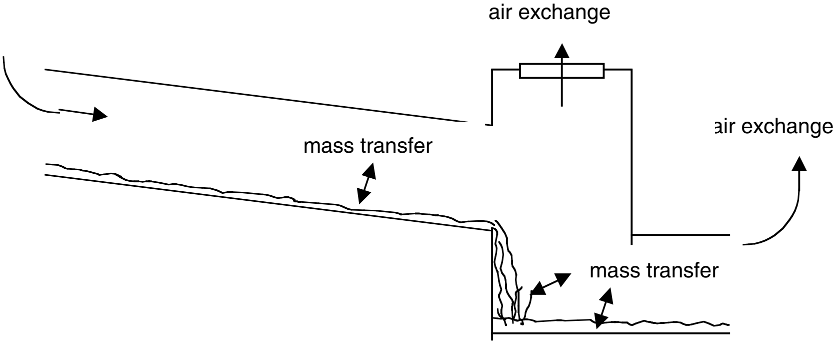


FIGURE 6.1 Schematic of emission mechanisms.

6.4 THEORETICAL CONSIDERATIONS

Gas–liquid mass transfer is typically modeled using either an equilibrium- or kinetics-based approach. An equilibrium approach assumes that chemical equilibrium exists between liquid and adjacent air. For such a condition, the emission rate of a specific chemical can be estimated as shown in Equation 6.1:

$$E = Q_g C_l H_c \tag{6.1}$$

where

E = emission rate for a chemical of interest (g/s)

Q_g = air flow rate exhausting from an opening in the sewer system (m^3/s)

C_l = chemical concentration in the liquid phase (g/m^3)

H_c = Henry's law constant for a chemical of interest (m^3_{liq}/m^3_{gas})

Equation 6.1 must be coupled with a mass balance on the liquid phase in order to account for spatial changes in C_l.

For a kinetics-based approach, the transfer of a chemical from the liquid to gas phase can be expressed as shown in Equation 6.2:

$$R_v = K_L A\left(C_l - \frac{C_g}{H_c}\right) \tag{6.2}$$

where

R_v = rate of mass transfer from liquid to gas (g/s)

K_L = overall mass transfer coefficient (m/s)

A = surface area between liquid and adjacent gas (m^2)

C_g = chemical concentration in the gas phase (g/m^3)

The term in the parentheses of Equation 6.2 is referred to as the concentration driving force. It is influenced by the following factors: the rate of mass transfer, which affects C_l and C_g; ventilation rate, which affects C_g; and temperature and chemical properties, which both affect H_c. Since it is sometimes difficult to experimentally separate the overall mass transfer coefficient (K_L) and interfacial area (A), these terms are sometimes "lumped" together as K_LA, e.g., in the case of drop structures. Equation 6.2 is the link between mass balances completed on both the liquid and gas phases of a sewer reach or other sewer components. These mass balances are used to solve for C_g, with subsequent estimation of emissions as the product of Q_g and C_g, i.e., $E = Q_gC_g$.

The inverse of the overall mass transfer coefficient ($1/K_L$) is referred to as the overall resistance to mass transfer. In accordance with the two-film theory,[17] this term can be subsequently separated into liquid- and gas-phase resistances to mass transfer as shown in Equation 6.3:

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{k_g H_c} \tag{6.3}$$

where

k_l = liquid-phase mass transfer coefficient (m/s)

k_g = gas-phase mass transfer coefficient (m/s)

Values of k_l and k_g are largely dependent on the turbulent kinetic energies of the liquid and gas phases, respectively, and, to a lesser extent, the molecular diffusion coefficients of a chemical in the liquid and gas phases.

An additional way to describe the emissions from sewers is to assume that the system approaches an open trench. For this method, it is assumed that the chemical accumulation in the gas phase to be negligible. It has been shown that the stripping efficiency (percent mass emitted to the ambient atmosphere) for a sewer approaching open trench conditions can be written as shown in Equation 6.4:[12]

$$\eta = 1 - \exp\left[-\frac{K_L WL}{Q_l}\right] \tag{6.4}$$

where

η = stripping efficiency (percent of mass removed from wastewater to air) (–)

W = width of the air-water interface (m)

L = sewer length (m)

This approach is most appropriate under conditions of high air exchange rates or high compound Henry's law constant.

Parkhurst and Pomeroy[13] were the first researchers to develop a model describing mass transfer along sewer reaches. They completed 12 experiments aimed at quantifying oxygen transfer in operating sewers under near-uniform flow conditions. Experiments were completed after shock loading of caustic soda and continuous addition of hypochlorite to minimize the effects of biological activity. A semi-empirical expression for the liquid-phase mass transfer coefficient for oxygen absorption in municipal sewers was developed as shown in Equation 6.5:

$$k_{lO_2} = 2.67 \times 10^{-4}(1 + 0.17\ \mathrm{Fr}^2)\gamma(SU)^{3/8} \tag{6.5}$$

where

k_lO_2 = liquid-phase mass transfer coefficient for oxygen (m/s)

Fr = Froude number (–)

$$\mathrm{Fr} = U/(gd)^{1/2}$$

U = wastewater velocity (m/s)

g = acceleration due to gravity (9.81 m/s^2)

d = depth of flow (m)

γ = temperature correction factor

$$\gamma = 1.024^{(t-20)}$$

t = liquid temperature (°C)

S = slope of the reach (m/m)

Another expression for the liquid-phase mass transfer coefficient for oxygen has been developed by Owens et al,.[14] as shown in Equation 6.6:

$$k_{1O_2} = 2.67 \times 10^{-5}\left(\frac{A_c}{W}\right)U^{0.67}d^{-1.85} \tag{6.6}$$

where

A_c = cross-sectional area of water flow (m^2)

This correlation was developed using experimental data from natural water streams.

Drop structures are also locations where mass transfer can occur. Though emissions can occur via several different mechanisms (implying several different mass transfer coefficients), these effects are typically combined into one oxygen transfer parameter called the oxygen deficit ratio,[15] as shown in Equation 6.7:

$$r_{O_2} = \frac{C_{so} - C_{1o}}{C_{so} - C_{2o}} \tag{6.7}$$

where

r_{O_2} = deficit ratio for oxygen (–)
C_{so} = dissolved oxygen concentration at saturation (mg/L)
C_{1o} = dissolved oxygen concentration upstream of a drop (mg/L)
C_{2o} = dissolved oxygen concentration downstream of a drop (mg/L)

The oxygen deficit ratio can be related to VOCs by Equation 6.8:[15]

$$r_{VOC} = r_{O_2}\psi_T = \frac{C_g/H_c - C_{1v}}{C_g/H_c - C_{2v}} \tag{6.8}$$

where

r_{VOC} = deficit ratio for VOC (–)
C_{lv} = chemical concentration in the liquid phase upstream of a drop (g/m^3)
C_{2v} = chemical concentration in the liquid phase downstream of a drop (g/m^3)

The derivation of Equation 6.8 has been described elsewhere.[15] The parameter ψ_T is the ratio of VOC and oxygen overall mass transfer coefficients and can be determined as shown in Equation 6.9:

$$\psi_T = \psi_L\psi_G\left(\frac{H_{VOC}}{H_o}\right)\left[\frac{1 + \left(\frac{K_g}{k_l}\right)_o H_o}{\psi_L + \psi_G H_{VOC}\left(\frac{K_g}{k_l}\right)_o}\right] \tag{6.9}$$

where

ψ_L = ratio of liquid-phase mass transfer coefficients of VOC and oxygen (–)

$$\psi_L = \left(\frac{D_{lVOC}}{D_{lO_2}}\right)^{\delta}$$

$D_{l\,VOC}$ = liquid-phase diffusion coefficient of VOC (cm^2/s)

D_{lO_2} = liquid-phase diffusion coefficient of oxygen (cm^2/s)

ψ_G = ratio of gas-phase mass transfer coefficients of VOC and oxygen (–)

$$\psi_G = \left(\frac{D_{gVOC}}{D_{gO_2}}\right)^{\delta}$$

$D_{g\,VOC}$ = gas-phase diffusion coefficient of VOC (cm^2/s)

D_{gO_2} = gas-phase diffusion coefficient of oxygen (cm^2/s)

H_{VOC} = Henry's law constant of VOC ($m_{liq}{}^3/m_{gas}{}^3$)

H_o = Henry's law constant of oxygen ($m_{liq}{}^3/m_{gas}{}^3$)

Values of δ can vary theoretically from 0.5 for surface renewal and penetration theories[16] to 1.0 for two-film theory.[17] Typically, a value near 2/3 is chosen. The oxygen deficit ratio can be estimated using an empirical relationship developed by Nakasone[18] and shown in Equation 6.10:

$$r_o = \exp\left(h^e q^b y^j\right) \tag{6.10}$$

where

h = drop height (m)

q = flow rate per unit width of drop (m^3/h/m)

y = tailwater depth (m)

W,e,b,j = empirical constants (listed in original reference)

6.5 TRACER STUDIES

A few studies have been completed where liquid tracers were injected into sewers with measurements collected downstream to back-calculate mass transfer coefficients over short reaches of sewer, e.g., 100 to 200 m. For example, Corsi et al.[19] released deuterated chloroform in two operating sewers in California. Both liquid and gas measurements were collected. In addition, the inert tracer sulfur hexafluoride (SF_6) was injected in the headspace so that gas flow rates could be estimated from the dilution of SF_6. Experimental average steady-state conditions were within 30% of gas-phase concentrations predicted using the mass transfer correlation developed by Parkhurst and Pomeroy.[13]

Jensen and Hvitved-Jacobsen[20] completed a series of experiments in operating sewers involving controlled injection of krypton. Experimental results from this study were also consistent with those predicted using the correlation developed by Parkhurst and Pomeroy.[13]

Whitmore and Corsi[21] completed four experiments in two operating sewers using deuterated chloroform and 1,1,1-trichloroethane as volatile tracers. The air headspace of the sewers was force-ventilated using a small blower. Both the tracer mixture and rhodamine dye were injected into the wastewater, while the inert tracer sulfur hexafluoride (SF_6) was injected into the headspace. Liquid and gas flow rates were estimated from the dilution of rhodamine and SF_6, respectively. Liquid mass transfer coefficients were between 0.014 and 0.15 m/hr and were generally within 30% of predicted values that were estimated using the correlation developed by Parkhurst and Pomeroy.[13]

The studies described above were all completed in large-diameter municipal sewers and typically involved highly volatile tracers that precluded any attempts to separate gas and liquid-phase mass transfer coefficients. A systematic study of liquid- and gas-phase mass transfer coefficients along sewer reaches was recently completed on a pilot-scale reach by Koziel.[22] The experimental reach was 61 m in length and 20 cm in inside diameter. A small drop structure (< 0.3 m) was allowed at the end of the reach to assess losses due to dissipation in potential energy that occurs at junction boxes and the connection of building laterals to street sewers. The system was also designed to allow for variations in water flow rate, channel slope and headspace ventilation rates. The latter could be established as either co-current or counter-current flow. Over the course of 20 experiments, channel slopes were varied from 0.5% to 2%, water flow rates were varied from 0.3 L/s to 3 L/s and air-to-liquid flow ratios ranged from 1.6 to 18.

Five volatile tracers (acetone, ethyl acetate, toluene, ethylbenzene, cyclohexane) with a wide range of chemical properties were used during each experiment. The extent of chemical stripping (stripping efficiencies) from the 61 m reach was determined to be extremely sensitive to both chemical properties and sewer operating conditions. For all 20 experiments, stripping efficiencies ranged from 0.3 to 2.2% for acetone, 0.8 to 5.6% for ethyl acetate, 5 to 41% for toluene, 4 to 41% for ethylbenzene and 11 to 47% for cyclohexane. For each experiment, as expected, stripping efficiencies generally increased with increasing Henry's law constants.

Results demonstrated the sensitivity of chemical emissions to chemical properties and sewer operating conditions and underscored the fact that a significant fraction of VOCs can be emitted from short sections of sewer reaches, e.g., those dominated by industrial discharges such as petroleum wastes. This is particularly true for chemicals with Henry's law constant greater than or equal to that for toluene. Furthermore, stripping efficiencies for the small drop structure located downstream of the experimental reach were similar in magnitude to those observed for the reach itself, thus increasing emissions from a combined reach and junction box or lateral connection. It should be noted that this experiment was designed to simulate the conditions that can be expected to occur immediately downstream from discharges at a petroleum refinery.

Concentration profiles in both the gas and liquid phases along the pilot-scale reach were used to determine values of liquid- and gas-phase mass transfer coefficients for each chemical and experiment. For all the 20 experiments conducted, values of k_l ranged from 1.8×10^{-5} m/s to 1.4×10^{-4} m/s. Similarly, gas-phase mass transfer coefficients ranged from 1.4×10^{-4} m/s to 4.9×10^{3}m/s. A correlation was developed for k_l as shown in Equation 6.11:

$$k_l = 6.25\ Sc_l^{-0.10}\ d^{\ 0.68}\ (U \times S)^{0.35} \tag{6.11}$$

where

k_l = liquid-phase mass transfer coefficient (m/s)
Sc_l = liquid-phase Schmidt number (–)
d = mean depth of flow = cross-sectional area/width (m)
U = water mean velocity (m/s)
S = channel slope (m/m)

The ratio of k_g to k_l was observed to be 29 based on an average of all experimental results. Caution should be exercised in using this ratio for all sewer reaches, because the concentrations of VOCs used in this study may not occur in actual field conditions. Hence, this estimate might not truly reflect the actual emissions because it does not represent actual conditions that exist in typical municipal collection systems. Most sewers do not transport wastes that contain a large fraction of industrial discharges containing high concentrations of VOCs; caution should be exercised in generalizing that sewers in all communities are major sources of VOC emissions.

6.6 FIELD MONITORING

Quigley and Corsi[24] measured VOCs from a municipal sewer that received discharges from a significant number of industrial sources including petroleum refinery wastes. The reach studied had a total length of 1.6 km, pipe diameters ranging from 0.9 to 1.2 m, 4 drop structures and 17 manholes (typically with highly perforated covers). Five VOCs were targeted for the study: benzene, toluene, ethylbenzene, total xylenes and tetrachloroethane. Emission rates (summed across four manholes) were the highest for toluene and approached a maximum of 100 g/hr. Average and maximum total nonmethane hydrocarbon emissions from one manhole for one 24-hr sampling event were 265 and 630 g/hr, respectively. Two large drop structures were observed to be a major source of emissions, leading to between 29 and 44% stripping for the chemicals studied. Headspace ventilation rates were as high as 2300 m^3/h, which was noted to be significantly higher than previously published values. It should be noted that the sewer line investigated in this study is not a typical representation of sewers of a collection system serving major metropolitan areas conveying mostly domestic sewage

6.7 DROP STRUCTURES

Well-ventilated sewer drop structures have been identified as sources of high VOC emissions if the contents of the indigenous wastewater are highly volatile.[25]

Several mass transfer mechanisms occur in drop structures. These include:

- Air bubbles entrained in the tailwater
- Agitated tailwater surfaces
- Splashing and airborne droplets formed due to the impact of a falling water set on the tailwater surface
- The free falling jet film surface
- Surface of the water

Because of these various mechanisms, it is difficult to determine the surface area associated with each of these mechanisms and, due to the non-uniformity of the gas phase, VOC concentrations in such systems.[19]

An overview of the approaches made for the modeling of VOC emissions of drop structures has been presented by Bell et al.[11] These include:

- The Ψ concept, Nappe model, which uses oxygen transfer data to relate to VOC deficit ratios and predict VOC emissions
- The Ψm model, which incorporates the contribution of gas phase mass transfer coefficient, VOC deficit ratios and the Henry's law coefficients
- The pool model, which presumes that most of the VOC mass transfer occurs to and from the entrained air bubbles, that the liquid phase is uniformly mixed and that the plug flow conditions exists in the gas phase and also uses VOC
- Deficit ratios, a mechanistic component model assuming that VOC emissions due to each of the mechanisms are additive[25]
- A lumped system model, which proposes a single mass transfer coefficient that accounts for all the above mechanisms[19]
- An air entrainment model, which assumes that mass transfer of VOCs occurs mostly due to air entrainment[19]

The Ψ_M concept, Nappe and Ψ_M models overpredict VOC emissions because of the inaccuracy of the assumptions made, namely, the VOC transfer occurs to and from the falling water and at the surface of the downstream water pool of a drop structure. The gas phase resistance of the VOCs is negligible and the ventilation rate is infinite. In the case of the pool model, there is a lack of knowledge of air entrainment rates and the degree of saturation of the VOCs in the entrained air bubbles.

Corsi and Quigley[15] conducted a series of 17 experiments on a pilot-scale drop structure. Between five and ten chemical tracers were used for all experiments. Resulting stripping efficiencies were found to be highly dependent on Henry's law constant, drop height, headspace ventilation rate and liquid flow rate. Stripping losses of VOCs ranged from 1 to 40%. An approximately linear relationship was displayed between stripping efficiency and any of the following parameters: Henry's law constant, drop height and headspace ventilation rate. Since wastewater typically flows over several drop structures before reaching a wastewater treatment plant, the study indicates that a significant fraction of VOCs can be emitted from collection systems before reaching the treatment plant.

6.8 AIR EXCHANGE RATES

The air exchange (ventilation) rate between the sewer and the ambient atmosphere is an important factor in estimating emissions from sewers. For an equilibrium-based approach (Equation 6.1), the emission rate is directly proportional to the air exchange rate. For a kinetics-based approach, the ventilation rate can affect both the gas-phase accumulation term (C_g/H_c in Equation 6.2) and the gas-phase mass transfer coefficient (k_g). Previous research has identified five mechanisms that can affect ventilation:

1. Liquid drag
2. Wind eduction
3. Buoyancy
4. Barometric pressure
5. Rise and fall of wastewater[26–32]

Pescod and Price[28,29] were the first researchers to conduct a series of experiments quantifying natural ventilation in sewers. They conducted experiments on a 0.30 m-diameter open-ended laboratory sewer pipe to study the effects of liquid drag. Air velocities were measured using an anemometer. Velocity measurements were taken at several locations over the air headspace cross-section to develop air velocity profiles for each experiment. Proportional water depths were varied from 0.25 to 0.75 and mean water velocities were varied from 0.2 m/s to 0.8 m/s.

The air velocity decreased exponentially with increasing vertical distance from the water surface (except near the pipe wall) and the air velocity at the surface was always slightly less than the average water velocity. Mean air velocities ranged from 0.11 m/s to 0.21 m/s. Average air velocities were reasonably correlated with the product of water surface velocity and a shape ratio. Flow conditions based on Reynolds number were generally in the transitional region, i.e., between laminar and turbulent flow conditions.

Bell et al.[11] in a recently reported study constructed a model for headspace gas flow velocity of the form shown below.

$$vg = av^b_w - c\omega^d,$$

where,

vg = headspace gas velocity, m/s

vw = water velocity in reach, m/s

ω = surface wind velocity over reach opening, km/h

a, b, c, d= model fitting constants

In this model, the water velocity and wind-induced suction affect the ventilation rate, unlike the suggestion made in the work of Pescod and Price.[29]

Predicted headspace gas velocities in two sewer reaches were compared by Bell et al.[11] with measured values of gas velocities in the same sewers. Also for comparison purposes, they used the full-scale data of Pescod and Price[29] and Quigley and Corsi[23] and the headspace gas velocities predicted by their model. These predicted and observed values are summarized in Table 6.1. The predicted-to-observed gas velocity ratios range from 3 to 5 and these high ratios indicate that the model overpredicts the gas velocity in the sewer reach headspace and hence the overprediction of VOC emission rates.

From their overview of the above modeling approaches, these authors have concluded that, while the developments of models to predict oxygen uptake seem to be relatively easy, serious limitations exist to relate oxygen uptake rate to the stripping of VOCs. The Nappe model overestimates the VOC emissions and cannot be applied to semivolatile compounds. A paucity of knowledge of the ratios of the liquid and gas phase mass transfer coefficients of VOCs limits the application of the ΨM models. Serious errors in the prediction of VOC losses by these models can be induced by inaccuracies of the assumptions made, namely: (1) VOC transfer occurs to and from the falling water and at the surface of the downstream water pool of a drop structure, (2) gas phase resistance of the VOCs is negligible and (3) ventilation rate is infinite can induce.

Information on the knowledge of air entrainment rates and the degree of saturation of the VOCs in the entrained air bubbles is seriously lacking in the application of the pool model and need to be obtained. In the case of the mechanistic model, also, serious weaknesses exist for the quantitation of air entrainment rates and degree of saturation of VOCs. Also, it is difficult to estimate mass transfer coefficients and effective surface areas for each of the VOC removal mechanisms included in this model. The lumped system and air entrainment models also suffer from a few or many of the above deficiencies.

TABLE 6.1
Predicted and Measured Headspace Gas Velocities in Full-Scale Reaches

Measurement	Bell et al. (1998)			Pescod and Price (1983)			Quigley and Corsi (1995)
Wind Velocity (km/h)	15	9.3	16.6	12.6	14.4	36.0	10
Water Velocity (m/s)	0.955	0.727	0.748	0	0.4	1.0	1.43
Predicted Gas Velocity (m/s)	0.536	0.370	0.512	0.268	0.385	0.910	0.572
Observed Gas Velocity (m/s)	0.106	0.110	0.172	0.0445	0.0358	0.145	0.206
Ratio Predicted: Observed Gas Velocity	5.06	3.37	2.97	5.97	10.8	6.29	2.78

To address the above deficiencies of the various models mentioned above, Bell et al.[11] conducted experiments using a pilot drop structure (1.22 m diameter × 1.3 m height) and attempted to predict VOC emissions with the Nappe, QM and the

Pool models (Bell et al.[11]). They studied the emissions of ten VOCs having a broad range of chemical properties (compounds with values ranging from 0.024 to 0.607), a tail water depth of 0.5 m with drop heights ranging from 0.42 to 1.67 m, liquid flow rates ranging from 4 to 12 m^3/h) and ventilation rates ranging from 7.8 to 39.5 m^3/h.

From these experiments, the following conclusion were drawn:

- Drop height increased, as did the stripping of VOCs. VOCs having higher H values stripped more than VOCs with lower H values.
- VOC removals exceeded 40% in the pilot drop structure, suggesting that drop structures of a collection system transporting wastewater containing high concentrations of VOCs can be significant sources of VOC emissions.
- The effect of liquid flow rate on VOC stripping could not be discerned.
- VOC stripping increased as the ventilation rate increased.
- The Nappe model overestimated VOC emissions.
- Although the ΨM model accurately predicted VOC stripping in clean water drip structures, it underpredicted in wastewater drip structures.
- Development of the Pool model was abandoned due to scatter and inconsistency in the data collected with the pilot drop structure.

Although these experiments indicated that the flow rate of wastewater does not have a bearing on VOC emission, the following mechanistic model described by Bell et al.[11] seem to indicate that the flow rate has an effect on the VOC mass transfer rate as shown in Equation 6.12:

$$E = \frac{C_{win}\left(Q_w\gamma_1 + K_2A_{dd} + K_3A_{sd} + k_4A_{surf} + Qe\gamma_2^H\right)}{\left[\dfrac{1 + Q_w\gamma_1 + K_2A_{dd} + K_3A_{sd}}{Q_a^H} + \dfrac{Qe\gamma_2^H + K_3A_{sd} + K_4A_{surf} + Qe\gamma_2^H}{Q_w}\right]} \tag{6.12}$$

where

E = Total emission

C_{win} = Concentration of VOC in the influent, gm^3

Q_w = Wastewater flow rate (m^3/sec)

γ_1 = Degree of equilibrium achieved during water fall (dimensionless, typical value = 0.05, range 10^{-5} to 5)

K_2 = Overall liquid mass transfer coefficients for disintegrating droplets (m/s)

A_{dd} = Total area of disintegrating waterfall droplets (cm^2)

K_2A_{dd} = m^3/s: Typical value = 0.005 QW; Range: 10^{-5} QW to 0.3 Q_W

K_3 = Overall liquid mass transfer coefficient for splashing droplets (m/s)

A_{sd} = Total area of splashing droplets (m^2)

K_3A_{sd} = (m^3/s): Typical value = 0.005 QW; Range: 10^{-5} Q_W to 0.3 Q_W

K_4 = Overall mass transfer coefficient for tailwater surface (m/s)

A_{surf}: = Tailwater surface area (m^2)

K_4A_{surf} = (m^3/s): Typical value = 0.005 Q_W; Range: $10^{-5}Q_W$ to 0.3 Q_W

Q_e = Rate of air entrainment (m^3/sec); Typical value: 10QW; Range: $1Q_W$ to $30Q_W$

γ_2 = degree of saturation of the entrained air bubbles prior to resurfacing (dimensionless); Typical value = 0.5, Range: 0.1 to 1.0

H = Henry's law coefficient

Q_a = Gas flow rate out of drop structure headspace (m^3/s); Typical Value = 10^{20}; Range 0.0025 to 10^{20}

Wastewater flow rate can approach zero or can exceed hundreds of millions of gallons per day as in big interceptor and trunk sewers. Also, H values for VOCs vary between 0.1 compounds like the dichloromethane to 2.5 for highly volatile compounds.

A summary of the predicted emissions based on the use of typical values given for the parameters contained in the mechanistic model suggests that 73% of VOCs were stripped. Also, it was predicted that 1 and 98% of the VOCs were stripped when the minimum and maximum values of the parameters were considered. The dominant and controlling mechanism for VOC losses for the "typical" and "minimum" value condition was air entrainment. More than 90% of the VOC losses were attributable to this mechanism under a wide range of conditions. Sensitivity analysis by these investigators also indicated that a small change in the wastewater flow rate, influent VOC concentration and the product of the mass transfer coefficient and the surface area of each of the influencing components will have the greatest effect on emission estimations. Field validation of this model under different conditions needs to be performed to ascertain VOC emissions with any degree of credibility. Unless extensive validation of the VOC emission rates reported from the above studies is done, it is not prudent to use these emission rates to compute the VOC emission rates for real life collection systems to assess any environmental impacts.

The largest study to date on ventilation in sewers was completed by Olson et al.[33,34] and involved both theoretical modeling and observations made in over 100 experiments completed on a laboratory-scale sewer system. The study differed from previous attempts to estimate sewer ventilation rates in that modeling efforts were based on fundamental fluid mechanics and heat transfer principles. Estimation of air exchange rates in a drain network was addressed theoretically by applying the first law of thermodynamics. A simplified form of the first law applicable to sewers can be written as (Olson et al.[33]) as shown in Equation 6.13:

$$\dot{q}_{net} = \dot{w}_{net} + \dot{m}_{air}\left(e+\frac{V^2}{2}\right)_{out} - \dot{m}_{air}\left(e+\frac{V^2}{2}\right)_{in} + \dot{m}_{air} g h_L \tag{6.13}$$

where

$\dot{q}_{net}$ = net rate of heat flow to/from the gas phase in a sewer (J/s)

$\dot{w}_{net}$ = net rate of work done on the gas phase in a sewer (J/s)

$\dot{m}_{air}$ = mass flow rate of air through a sewer reach or other sewer component (kg/s)
e = enthalpy of air (J/kg)
V = velocity of air (m/s)
subscript "out" = outlet air conditions
subscript "in" = inlet air conditions
g = acceleration due to gravity (9.81 m/s^2)
h_L = gas-phase headloss through the drain network (m)

Use of Equation 6.13 to estimate ventilation rates from industrial process drains was verified for 109 laboratory-scale experiments over a range of environmental conditions. Experiments were designed to isolate the effects of liquid drag, buoyancy and wind education. A series of experiments was also completed to study both additive and competitive ventilation mechanisms. A detailed discussion on the derivation of Equation 6.13, model parameters used for each ventilation mechanism and experimental methodology is provided by Olson et al.[33] A major conclusion from this research is that buoyancy and wind education are the dominant ventilation mechanisms for industrial process drains. Measured and predicted values were always within a factor of two and generally within ±30% of one another. Approximately 50% of all predicted air exchange rates were within 10% of measured values. The applicability of this model has not been evaluated for municipal sewers, which are much more complicated than a laboratory controlled sewer system. Hence, any predicted VOC emission rate cannot be extrapolated to a complex sewer network system of large municipal agencies without a complete validation of the models developed.

Parker and Ryan[35] measured ventilation rates from an operating municipal sewer using carbon monoxide as a tracer gas. The sewer was approximately 11 km long with pipe diameters ranging from 0.61 to 2.1 m and had several manholes and drop structures. Headspace velocities ranged from 3.6 to 31.5 m/min. Ventilation rates generally increased with downstream location, a phenomenon attributed to increased wastewater drag.

6.9 MODELING

6.9.1 SCREENING TECHNIQUES

A novel screening approach developed by Koziel and Corsi[36] uses chloroform as an *in situ* tracer. The chloroform mass balance approach requires the following parameters: chloroform concentrations entering the collection system, chloroform concentrations entering the wastewater treatment plant, water flow rates and VOC concentrations entering the collection system. Chloroform losses through the system are attributed to air emissions and an effective stripping efficiency is then back-calculated. The system-wide VOC emission rate can then be estimated knowing the VOC concentration entering the wastewater treatment plant.

This approach was used to estimate total emissions of eight volatile HAPs (benzene, chloroform, dichloromethane, ethylbenzene, tetrachloroethene, toluene, 1,1,1-trichloroethane and total xylenes) in Dallas and New York City sewers.[10] Emissions of only these HAPs were predicted to range from 13 to 92 metric tons per year (mtpy) for Dallas and from 67 to 326 mtpy for three systems in New York City. In each case, the percentage of volatile HAPs stripped (removed) from sewers prior to reaching a wastewater treatment plant ranged from 76 to 96% and 86 to 97% in the Dallas and New York City systems, respectively. The emission estimates reported by Corsi need to be validated by actual measurements made in the collection systems of these cities for an accurate assessment of the environmental and health impacts.

Although this method provides a relatively simple way to estimate system-wide mass emission rates using data available to most municipalities, the major limitation is that the method assumes that discharges are uniformly discharged, an assumption that is reasonable for widely discharged chemicals such as chloroform, but may be inappropriate for other VOCs. The actual VOC emission rates from a municipal collection system still remain a complex issue.

Another screening method was developed by Olson et al.[12] It involves a combination of the equilibrium and open-trench approaches described above. The method is considerably more accurate than an exclusively equilibrium- or open-trench-based approach. It was shown mathematically that the maximum error between the combined approach and a co-current ventilation (most sophisticated) approach is 58% and independent of reach and flow characteristics. The method still requires knowledge of the magnitude and direction of air flow through the network. Although considerable work has been done, the determination of the actual VOC emission rates from a municipal collection system still remains a complex issue and any predicted VOC emissions can be considered highly conservative and need validation by actual measurements.

6.9.2 CORAL+

The CORAL model was the first commercially available model for estimating emissions from sewer reaches.[19] This was subsequently expanded and upgraded to CORAL+. It can estimate emissions from a single sewer reach and drop structure for both continuous and dynamic VOC discharges. Liquid-phase mass transfer coefficients are estimated using the oxygen transfer correlation developed by Parkhurst and Pomeroy[13] with diffusivity-based adjustment between oxygen and the VOC of interest. Required inputs include the ventilation pattern (co-current or uniform) and air exchange rate. Emissions from drop structures are estimated using the oxygen deficit ratio correlation developed by Nakasone.[18] Also, this model can be used to demonstrate how significant passive reductions in VOCs can be obtained by controlling system parameters such as sewer channel slope, relative depth of flow, pipe diameter and head space ventilation rate.[37] The CORAL+ model has been used to estimate emissions of six volatile HAPs (benzene, dichloromethane, ethylbenzene, toluene, 1,1,1-trichloroethane and o-xylene) from sewers in Chicago.[38] A total emissions estimate of 270 mtpy was predicted.

6.9.3 WATER9

Using the WATER9 model, liquid-phase mass transfer coefficients can be selected from three correlations[14,13,39] with diffusivity-based adjustment to VOCs. For drop structures, WATER9 uses the oxygen deficit ratio correlation developed by Nakasone.[18] Based on the work done by Bell et al.,[11] this approach overpredicts the VOC emissions from sewers.

6.9.4 TOXCHEM+

The approach TOXCHEM+ uses to estimate emissions from reaches and drop structures is similar to that used by CORAL+, except that emissions from multiple reaches and drops can be simulated.

6.9.5 naUTilus

The naUTilus model incorporates results from many of the studies described above. A detailed description of the naUTilus model is provided elsewhere.[40] This model was originally intended for industrial sewers. Whether this model can also be applied to municipal sewer systems needs further investigation. The model estimates emissions from entire sewer networks from point of origin to the influent of a wastewater treatment plant. It allows for linkage of multiple process units to a centralized industrial collection system. An important feature of the model is its ability to estimate air exchange rates given system operating and environmental conditions. The naUTilus model can be used to provide a detailed emission inventory for an entire sewer system and for the mechanistic analysis of the effects of system modifications on the magnitude and spatial distribution of VOC emissions.

6.10 Summary

As suggested in this chapter, a significant fraction of VOC discharges to sewers appears to be emitted from collection systems before reaching a wastewater treatment plant. Given the comparatively high stripping efficiencies for both steeper, smaller diameter laterals drop structures and other sewer appurtenances, it is likely that, for most VOCs, emissions from collection systems are at least as great and probably greater than emissions from treatment systems. Although significant advances have been made toward estimating volatile HAP emissions from municipal sewers, several uncertainties continue to exist and must be resolved before this source can be rigorously assessed relative to other sources before any regulatory action is taken.

While the potential for significant HAP emissions from municipal sewers appears to be great, such emissions have neither been directly measured nor confirmed through a rigorous and systematic field study. Though a few computational models exist for estimating VOC emissions from municipal sewers, little work that compares model results with field monitoring studies has been completed. Since the large number of openings makes routine monitoring of entire sewer networks cost prohibitive, assessments of VOC emissions from sewers often rely heavily on computational modeling. These models are useful for screening purposes and should be fully validated with field data.

Little is known about the distribution of emissions from entire sewer networks. If emissions are well distributed over the network, it is unlikely that VOC emissions from sewers pose a serious health threat. However, if emissions are isolated to only a few locations, such as drop structures, then such emissions may pose a health threat. Sensory observations may suggest that the latter case is more likely, since odor problems in sewers are often associated with localized points of high ventilation (typically drop structures and pump stations). However, it should be noted that odors are generally created by the degradation of sulfur-containing compounds and not necessarily by VOCs such as BTEX compounds and other chlorinated solvents.

Additional work is needed to better characterize air exchange rates in sewers. Further research that characterizes air flow patterns in sewer networks is needed. Both the magnitude and pattern of air flow in a network will have a significant effect on overall emissions.

Previous research has focused on liquid-to-gas mass transfer in sewers. However, some fraction of VOCs in sewers may be adsorbed to suspended solids, absorbed to oils (e.g., vegetable oil) or even biodegraded in biofilms attached to wetted sewer walls. While preliminary modeling indicates that mass transfer from wastewater to air is significantly more important than other loss mechanisms, additional (experimental) research is needed to study the effects of adsorption and biodegradation of VOCs in sewers.

REFERENCES

1. Austin, T., VOCs: The new effluent, *Civil Eng.*, 43–45, March 1992.
2. Bell, J.P., Melcer, H., Monteith, H.D., Osinga, I. and Steel, P., Stripping of volatile organic compounds at full-scale municipal wastewater treatment plants, *Water Environ. Res.*, 65(6), 708–716, 1993.
3. Corsi, R.L. and Card, T.R., Estimation of VOC emissions using the BASTE model, *Environ. Prog.*, 10(4), 290–299, 1991.
4. Cowan, C.E., Larson, R.J., Feijtel, T.C.J. and Rapaport, R.A., An improved model for predicting the fate of consumer product chemicals in wastewater treatment plants, *Water Res.*, 27(4), 561–573, 1993.
5. Govind, R., Lai, L. and Dobbs, R. Integrated model for predicting the fate of organics in wastewater treatment plants, *Environ. Prog.*, 10(1), 13–22, 1991.
6. Kyosai, S. and Rittmann, B.E., Effect of water-surface desorption on volatile compound removal under bubble aeration, *J. Water Pollut. Contr. Fed.*, 63(6), 887–894, 1991.
7. Melcer, H., Nutt, S.G. and Monteith, H., Activated sludge process response to variable inputs of volatile organic contaminants, *Water Sci. Techol.,* 23, 357–365, 1991.
8. Milhelic, J.R., Baillod, C.R., Crittenden, J.C. and Rogers, T.N., Estimation of VOC emissions from wastewater facilities by volatilization and stripping, *J. Air Waste Mgmt. Assoc.*, 43, 97, 1993.
9. Tata, P., Soszynski, S., Lordi, D.T., Zenz, D.R., Lue-Hing, C. and Card, T., Prediction of Volatile Organic Compound Emissions from Publicly Owned Treatment Works, *Proc. 68th Annual Water Environment Federation Conference*, Miami Beach, Florida, 1996.

10. Corsi, R.L., HAP emissions from municipal sewers: Should facilities and regulators be looking upstream? *Water Environ. Technol.*, 51–56, 1997.
11. Bell, J.P., Monteith, H.D., Parker, W.J., Corsi, R.I. and Zytner, R., Modeling the stripping and volatilization of VOC in wastewater collection and treatment systems, *Project 91-TFT-1 Report*, Water Environment Research Foundation, Alexandria, Virginia, 1998.
12. Olson, D.A., Varma, S. and Corsi, R.L., A new approach for estimating volatile organic compound emissions from sewers: methodology and associated errors. *Water Environ. Res.*, 70(3), 276–282, 1997b.
13. Parkhurst, J.D. and Pomeroy, R.D., Oxygen absorption in streams, *J. Sanitary Eng. Div., ASCE*, 98(SA1), 101–123, 1972.
14. Owens, M., Edwards, R.W. and Gibbs, J.W., Some reaeration studies in streams, *Int. J. Air Water Pollut.*, 8, 469–486, 1964.
15. Corsi, R. L. and Quigley, C. J., VOC emissions from sewer junction boxes and drop structures: Estimation methods and experimental results, *J. Air Waste Mgmt. Assoc.*, 46(3), 224–233, 1996.
16. Higbie, R., The rate of exposure of a pure gas into a still liquid during short periods of exposure, *Trans. Am. Inst. Chem. Eng.*, 31, 365–388, 1935.
17. Lewis, W.K. and Whitmann, W.G., Principles of gas absorption, *Indust. Eng. Chem.*, 16, 1215–1220, 1924.
18. Nakasone, H., Study of aeration at weirs and cascades, *J. Environ. Eng., ASCE*, 113(1), 64–81, 1986.
19. Corsi, R L., Chang, D.P.Y. and Schroeder, E.D., A modeling approach for VOC emissions from sewers, *Water Environ. Res.*, 64(5), 734–741, 1992.
20. Jensen, N.A. and Hvitved-Jacobsen, T., Method for measurement of reaeration in gravity sewers using radiotracers, *J. Water Pollut. Contr. Fed.*, 63(5), 758–767, 1991.
21. Whitmore, A. and Corsi, R.L., Measurement of gas–liquid mass transfer coefficients for volatile organic compounds in sewers, *Environ. Prog*, 13(2), 114–123, 1994.
22. Koziel, J.A., Corsi, R.L. and Lawler, D.F., Gas–liquid mass transfer along small sewer reaches, *ASCE J. Environ. Eng.*, in press, 2001.
23. Quigley, C.J. and Corsi, R.L., Emissions of VOCs from a municipal sewer, *J. Air Waste Mgmt. Assoc.*, 45(5), 395–403, 1995.
24. Corsi, R.L. and Quigley, C. J., Aromatic emissions from a municipal sewer interceptor, *Water Sci. Technol.*, 31, 7, 137–145, 1995.
25. Burnham, N., Corsi, R.L., Zytner, R. and Stiver, W.H., Model for VOC emissions at hydraulic drop structures, *Proc. Joint CSCE-ASCE National Conference on Environmental Engineering*, 1735–1742, 1993.
26. Pomeroy, R., The pros and cons of sewer ventilation, *Sewage Works J.*, 17(2), 203–208, 1945.
27. Thistlethwayte, D.K.B., *The Control of Sulphides in Sewerage Systems*, 1st ed. Ann Arbor Science Publishers, Ann Arbor, Michigan, 1972.
28. Pescod, M.B. and Price, A.C., Fundamentals of sewer ventilation as applied to the Tyneside sewerage scheme, *Water Pollut. Contr.*, 90(1), 17–33, 1981.
29. Pescod, M.B. and Price, A.C., Major factors in sewer ventilation, *J. Water Pollut. Contr. Fed.*, 54(4), 385–397, 1982.
30. U.S. EPA, VOC emissions from petroleum refinery wastewater systems — background information for proposed standards, EPA-450/3-85-001a, Research Triangle Park, North Carolina, 1985.
31. U.S. EPA, Control of volatile organic compound emissions from industrial wastewater, preliminary draft, Research Triangle Park, North Carolina, 1988.

32. Alpha-Gamma Technologies, Inc., Low emission sewer systems for industry, *Water Environ. Res. Found.*, Alexandria, Virginia, 1994.
33. Olson, D.A., Rajagopalan, S. and Corsi, R.L., Ventilation of industrial process drains: Mechanisms and effects on VOC emissions, *ASCE J. Environ. Eng.*, 123(9), 939–948, 1997a.
34. Olson, D.A., Corsi, R.L. and Rajagopalan, S., Ventilation of sewers: the role of thermal gradients, *Adv. Environ. Res.*, 1(3), 312–322, 1997c.
35. Parker, W.J. and Ryan, H., A tracer study of headspace ventilation in a collector sewer, *J. Air Waste Mgmt. Assoc.*, 51(4), 582–592, 2001.
36. Koziel, J.A. and Corsi, R.L., A novel approach for estimating VOC emissions from municipal sewers: Methodology, applications and implications, *Proc. 89th Annual Meeting of the Air and Waste Management Association*, Nashville, Tennessee, 1996.
37. Corsi, R.L., Birkett, S., Melcer, H. and Bell, J., Control of VOC emissions from sewers: A multiparameter assessment, *Water Sci. Technol.*, 32, 7, 147–157, 1995.
38. Jones, D.L., Burkin, C., Seaman, J., Jones, J.W. and Corsi, R.L., Models to estimate hazardous air pollutant emissions from municipal sewers, *J. Air Waste Mgmt. Assoc.*, 46(7), 657–666, 1996..
39. Mackay, D. and Yuen, A.T.K., Mass transfer coefficient correlations for volatilization of organic solutes from water, *Environ. Sci. Technol.*, 17(4), 211–217, 1983.
40. Olson, D.A. and Corsi, R.L., naUTilus: A model for predicting HAP emissions from industrial sewers, *Proc. 90th Annual Meeting of the Air & Waste Management Association*, Toronto, 1997.

7 VOC Emissions from Preliminary and Primary Treatment

Al Pincince

CONTENTS

7.1 Introduction 117
7.2 Emissions at Bar Racks or Screens 117
7.3 Grit Chambers 118
7.4 Clarifier Surface 119
7.5 Emissions at Clarifier Weirs 123
7.6 Summary 125
References 125

7.1 INTRODUCTION

Preliminary and primary treatment consists of physical processes to remove screenings, grit, grease and settleable suspended material. This chapter describes the units and mechanisms for emitting (VOCs). The discussion encompasses emissions from bar racks, grit chambers and settling tanks. For the latter, emissions are discussed for both clarifier surfaces and weirs.

7.2 EMISSIONS AT BAR RACKS OR SCREENS

Bar racks are used to remove screenings (rags, sticks and other material that might damage or clog equipment, pipes, or channels). The openings between bars in bar racks or screens range from about 10 mm to 150 mm. Emissions are caused by the turbulence as the flow passes between the bars from the upstream side to the downstream side.

The procedure developed by Meyerhofer et al.[1] can be used for estimating emissions from bar racks and Parshall flumes. A simplified mass balance expression for the rate of change of VOC concentration is shown in Equation 7.1:

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

$$\Delta C/\Delta t = K_L a_v C \tag{7.1}$$

where

ΔC = change in VOC concentration, (mg/l)
$K_L a_v$ = volumetric transfer coefficient for VOC (h^{-1})
C = influent VOC concentration, g/m^3
Δt = time of flow, h

As suggested by Tsivoglou and Neal,[2] the oxygen mass transfer rate constant can be expressed as a function of change of elevation and time of flow between two locations in a stream.

$$K_L a_0 = b\Delta h/\Delta t \tag{7.2}$$

where,

$K_L a_0$ = overall mass transfer coefficient for oxygen, (h^{-1})
b = escape coefficient, (m^{-1})
Δh = head loss across unit, m

The escape coefficient, b, is a function of flow characteristics and water quality. Tsivoglou and Neal[2] suggested an escape coefficient in the range of 0.08 to 0.10/m at 20°C for heavily polluted streams with flows larger than 0.7 m^3/s (15.98 MGD) for this analysis. They recommended an upper value of about 0.25 for lower flows and low pollution.

These two equations can be combined to yield Equation 7.3:

$$\Delta C = \Psi b \, \Delta h \, C \tag{7.3}$$

where

Ψ = mass transfer ratio, dimensionless
= $K_L a_v / K_L a_0$

7.3 GRIT CHAMBERS

Grit chambers can be classified as velocity controlled, aerated, vortex-type and detritus tanks.

Velocity-controlled grit chambers are channels with a weir or other device at the downstream end to maintain a constant velocity. These grit chambers have a high overflow rate because of their low surface area. Consequently, emissions from the surface are unimportant and most of the emissions are associated with turbulence at the velocity-control device. Emissions can be estimated using procedures developed for drop structures.[3]

In aerated grit chambers, spiral flow pattern with a horizontal axis is induced by supplying air from diffusers located on one longitudinal side of the tank. Emissions can be estimated using procedures described for aeration tanks with no biological activity. (See Chapter 9 for emissions from aeration tanks.) Alternatively, the entire tank can be covered and the offgas can be analyzed for VOCs.

Vortex-type grit chambers induce a vortex by inserting flow tangentially into a circular tank. Rotating paddles maintain circulation in the chamber and emissions from the surface are small. The major source of emissions is the point where the discharge spills into the exit channel.

Detritus tanks are square tanks with short detention times and high overflow rates. Emissions from the surface are small, but can be estimated using procedures described for primary clarifiers. Most of the emissions originate at the overflow weir. (See Section 7.5 for estimating emissions at weirs.)

7.4 CLARIFIER SURFACE

Emissions from a clarifier surface can be estimated by developing a mass balance including VOCs in the flow into the clarifier, in the flow just before it goes over the weir, those emitted from the surface and those adsorbed on the sludge. The mass balance is presented in Equation 7.4:

$$Q_L C_o = Q_L C_L + K_L A C_L + w K_p C_L \tag{7.4}$$

where

Q_L = liquid flow rate, m^3/d

C_o = influent VOC concentration in liquid, g/m^3

C_L = concentration of VOC in liquid in clarifier (and in effluent), g/m^3

K_L = overall mass-transfer coefficient for VOC, (Δ/T)

A = surface area of clarifier, m^2

w = rate of removal of sludge, g/d and

K_p = partition coefficient relating the fraction adsorbed to the concentration in the liquid (dimensionless).

This mass balance assumes that the concentration of VOC in the liquid is uniform and that the VOC concentration in the ambient air is low. This assumption that VOC concentration is uniform is valid for a completely mixed system or, in the case of a clarifier, where changes in concentration in the system are small.

As the adsorption of VOCs on sludge solids is negligible, the effluent concentration of the VOC is as shown in Equation 7.5:

$$\frac{C_L}{C_o} = \frac{1}{1 + \frac{K_L A}{Q_L}} \tag{7.5}$$

The fraction (f) emitted from the surface (not including the weir) is as shown in Equation 7.6:

$$f = \frac{\frac{K_L A}{Q_L}}{1 + \frac{K_L A}{Q_L}} \tag{7.6}$$

The overall mass transfer coefficient (K_L) [4] is a function of the liquid-film and gas-film mass-transfer coefficients and Henry's Law constant as shown in Equation 7.7:

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{k_G H_c} \tag{7.7}$$

where

k_L = liquid-film mass-transfer coefficient
k_G = gas-film mass-transfer coefficient
H_c = dimensionless Henry's Law constant

The mass-transfer coefficients depend on wind speed, properties of VOC, properties of air and water and basin geometry. Several correlations have been developed relating these properties. The correlations commonly used are according to Mackay and Yuen[5] and Springer et al.[6]

TOXCHEM+ uses correlations developed by Mackay and Yeun[5] for gas-film and liquid-film coefficient as shown in Equations 7.8, 7.9 and 7.10:

$$k_G = 1.0 \times 10^{-3} + 46.2 \times 10^{-3} \times U^* Sc_G^{-0.67} \tag{7.8}$$

$$k_L = 1.0 \times 10^{-6} + 144 \times 10^{-4} U^{*2.2} Sc_L^{-0.5} \left(U^* < 0.3\, m/s\right) \tag{7.9}$$

$$\begin{gathered} k_L = 1.0 \times 10^{-6} + 34.1 \times 10^{-4} U^* Sc_L^{-0.5} \left(U^* > 0.3\, m/s\right) \\ U^* = 10^{-2}\left(6.1 + 0.63 U_{10}\right)^{0.5} U_{10} \end{gathered} \tag{7.10}$$

where

k_G = gas phase mass transfer coefficient, m/s,
k_L = liquid phase mass transfer coefficient, m/s,
U^* = air side friction velocity, m/s,
U_{10} = wind velocity 10 m above the water surface, m/s,
Sc_G = gas phase Schmidt number, dimensionless,
Sc_L = liquid phase Schmidt number, dimensionless.

The Schmidt numbers are calculated as follows:

Sc_G = v_a ($D_G d_a$)

v_a = 0.17625
D_G = $0.0067T^{1.5}\,(0.034 + M^{-1})^{0.5}\,M^{-0.17}((M/2.5d_c))^{0.33} = 1.81)^{-2}$
d_a = 1.2928 (273.16/T)
Sc_L = $v_W/(D_L d_W)$
v_W = $(2.1482((T_c{-}8.435) + (8078.4 + (T_c - 8.435)^2)^{0.5}) - 120.0)^{-1}$
d_L = $5.06 \times 10^{-9}\, T d_c^{0.6} / M^{0.6}\, V_w$
d_w = 0.9982

where:

v_a = viscosity of air, g/cm s,
D_G = diffusion coefficient of compound in air, cm^2/s,
T = temperature, °K,
M = molecular weight of compound, g/mol,
d_c = density of compound, g/cm^3,
d_a = density of air, g/cm^3,
v_w = viscosity of water, g/cm s,
T_c = temperature, °C,
D_L = diffusion coefficient of compound in water, cm^2/s,
D_w = density of water, g/cm^3.

WATER8 uses correlations by Springer et al.[6] and by Mackey and Yeun[5] for the liquid-film mass-transfer coefficients. (See Table 7.1 showing when correlations are used.) The correlations by Springer et al.[6] are used for all cases except where the fetch-to-depth ratio is 3.25 and the wind speed at 10 m above the liquid surface exceeds 3.25 m/s. For that ratio, Mackey and Yeun's[5] liquid-phase mass-transfer coefficient (the one used by TOXCHEM+) is used. The correlations by Springer et al.[6] are shown in Equations 7.11, 7.12 and 7.13:

TABLE 7.1
Liquid-Film Mass-Transfer Correlation Used by WATER8

	Wind Speed 10 Meters Above Water Surface (m/s)	
Fetch/Depth	**<3.25**	**>3.25**
<14	Springer et al., Equation 11	MacKay and Yeun, 1983 Equations 7.9 and 7.10
14 to 51.2		Springer et al., 1984 Equation 7.12
>51.2		Springer et al., 1984 Equation 7.13

$$k_L = 2.78\times10^{-6}\left|\frac{D_w}{D_{ether}}\right|^{2/3} \left(0 < U_{10} < 3.25\right) \text{ All } F/d \text{ ratios} \quad (7.11)$$

$$k_L = \left[2.065\times10^{-9}(F/d) + 1.277\times10^{-7}\right]U_{10}^2\left|\frac{D_w}{D_{ether}}\right|^{2/3} \quad (7.12)$$

$$\left(U_{10} > 3.25\,\text{m/s}\right); \left(14 < F/d < 51.2\right)$$

$$k_L = 2.611\times10^{-7}U_{10}^2\left|\frac{D_w}{D_{ether}}\right|^{2/3} \left(U_{10} > 3.25\,m/s\right); \left(F/d > 51.2\right) \quad (7.13)$$

where

U_{10} = windspeed at 10 m above the liquid surface, m/s;
D_w = diffusivity of constituent in water, cm^2/s;
D_{ether} = diffusivity of ether in water, 8.5×10^{-6} cm^2/s; and
F/d = fetch-to-depth ratio (fetch is the linear distance across the impoundment).

In the gas-phase mass-transfer coefficient, WATER8 uses the following correlation by MacKay and Matsunaga[7] shown in Equation 7.14:

$$K_G = 4.82\times10^{-3}U^{0.78}Sc_G^{-0.67}d_e^{-0.11} \text{ (m/s)} \quad (7.14)$$

where

U = windspeed, m/s;
d_e = effective diameter of impoundment = $(4A)^{0.5}/\pi$, m;
A = surface area of impoundment, m^3
Sc_G = Schmidt number on gas side = $\mu_g / \rho_g D_a$;
μ_g = viscosity of air = g/cm s;
ρ_g = density of air, g/cm^3; and
D_a = diffusivity of a constituent in air, cm^2/s.

To estimate K_L, BASTE utilizes results of studies published by Cohen et al.[8], for volatilization of benzene and toluene from liquid baths placed in a wind tunnel. The value of K_L was observed to correlate well with wind speed at 10 cm above the liquid surface (U_{10}). For values of U_{10} less than or equal to 3 m/s, K_L is insensitive to U_{10} and equals to 8.3×10^{-6} m/s. For U_{10} between 3 m/s and 10 m/s, K_L equals 8.3×10^{-6} m/s and 8.3×10^{-5} m/s for $U_{10} = 3$ m/s and $U_{10} = 10$ m/s, respectively. Values of K_L for VOCs other than benzene and toluene are estimated by multiplying K_L for benzene (or toluene) by $\Psi voc/\Psi_{\text{benzene (or toluene)}}$.

Several studies have been conducted to determine the effect of wind on the mass-transfer coefficient of gases. In one of those studies, O'Connor[9] reviewed previous studies and correlated the mass-transfer coefficient for oxygen (K_{LO}) and wind velocity for small-scale, intermediate and field conditions. In this chapter, the correlation for intermediate conditions is given. This correlation is based on studies in facilities ranging from about 3 m to 18 m in length. (The small-scale studies were conducted on facilities generally under 3 m in horizontal dimension. The field studies were conducted on lakes and open ocean.) The liquid transfer coefficient for a VOC is equal to the liquid transfer coefficient for oxygen times the relative overall mass-transfer coefficient.

TOXCHEM+ used a relationship by Dobbs et al.[10] to estimate the partition coefficient as shown in Equation 7.15:

$$\log K_p = 0.58 \log K_{ow} + 1.14 \tag{7.15}$$

where

K_p = sorption partition coefficient, L/kg,
K_{ow} = octanol/water partition coefficient, dimensionless.

7.5 EMISSIONS AT CLARIFIER WEIRS

To date, studies aimed at providing procedures for estimating emissions of VOCs at clarifier weirs have focused on measurements of oxygen transfer with the intent of using relationships between oxygen transfer and transfer of VOCs to estimate VOC emissions. Two sets of experiments provide information on oxygen transfer at primary clarifier weirs.

Pincince[11] reported on studies at primary clarifiers at seven wastewater treatment plants. In the studies, oxygen concentrations taken upstream and downstream of clarifier weirs were correlated with weir loadings and drops. The relationship provided for emissions at primary clarifiers is shown in Equation 7.16:

$$\ln r_o = 0.042\, Z^{0.872}\, q^{0.509}, \tag{7.16}$$

where

r_o = deficit ratio at 20°C
Z = vertical distance from upstream water surface to downstream water surface
q = weir loading (m^3/m-m-h).

The deficit ratio is the ratio of the oxygen deficit upstream to the deficit downstream shown in Equation 7.17:

$$r_o = \frac{C_s - C_u}{C_2 - C_d} \tag{7.17}$$

where

r_o = deficit ratio, dimensionless;

C_s = saturation concentration for dissolved oxygen, mg/L;

C_u = concentration of dissolved oxygen upstream of the weir, mg/L; and

C_d = concentration of dissolved oxygen downstream of the weir, mg/L.

For temperature other than 20°C, a correction factor by Nakasone[12] can be used. The correction factor is shown in Equation 7.18:

$$\ln r_T = [1 + 0.0168^{(T-20)}] \ln r_o \tag{7.18}$$

where

T = water temperature, ˚C;

r_T = deficit ratio at temperature T.

Labocha et al.[13] determined deficit ratios for clean water and primary effluent in pilot-scale weir models. Their "modified V-notch weir," consisting of a broad-crested weir with a V-notch-shaped plate, was similar in cross-section to weirs usually used at wastewater treatment plants.

For clean water, they developed the relationship shown in Equation 7.19:

$$\ln r_o = 0.0045\, Z^{1.26} Q^{-0.09}, \tag{7.19}$$

where Q is the flow in L/min

For primary effluent, the relationship was developed as shown in Equation 7.20:

$$\ln r_o = 0.002\, Z^{1.36} Q^{-0.15}. \tag{7.20}$$

However, the clean-water equation with an a of 0.52 fit the data for primary effluent almost as well as Equation 7.20. With the α term, the equation for primary effluent, as shown in Equation 7.21, was:

$$\ln r_o = \alpha\, (0.0045\, Z^{1.26} Q^{-0.09}). \tag{7.21}$$

Pincince[11] suggested that information from dissolved oxygen measurements can be used to estimate emissions of VOCs by the relationship shown in Equation 7.22:

$$\ln r_v = \ln r_o\, (K_{Lv}/K_{Lo}) \tag{7.22}$$

where

$$r_v = \frac{\textit{concentration of VOC upstream}}{\textit{concentration of VOC downstream}}$$

$$r_o = \frac{\textit{concentration of DO upstream}}{\textit{concentration of DO downstream}}$$

The ratio K_{Lv}/K_{LO} is the ratio of the overall mass-transfer coefficient of VOC to the overall mass-transfer coefficient of oxygen. The value of K_{Lv}/K_{LO} can be obtained from experimental values or from relationships involving *diffusivities* or critical volumes. Matter-Muller et al.[14] state that this ratio is independent of temperature and the degree of turbulence, but Rathbun and Tai[15,16] show that the ratio increases for systems with low turbulence. Moreover, the relationship applies only to cases where, as with oxygen, the liquid film controls.

Mihelcic et al.[17] suggested that Equation 7.22 overestimates emissions. As an alternative, they suggested the relationship shown in Equation 7.23:

$$r_v = 1 + \frac{Q_G}{Q_L} H_v \left(1 - \exp\left(\left(\frac{D_V}{D_o} \right) \frac{H_o}{H_v} \ln\left(1 - \frac{r_o - 1}{\frac{Q_G}{Q_L} H_o} \right) \right) \right) \tag{7.23}$$

Equation 7.22 assumes that the concentration of VOC in air to which the VOC is transferred is negligible. Equation 7.23 assumes, on the other hand, that the mechanism for transfer of VOCs is via bubbles formed as the nappe splashes in the effluent launder. With bubbles formed, the transfer is affected by Henry's law limitations. These limitations occur because the concentration of VOC in the rising bubble limits the rate of transfer from the liquid to air.

7.6 SUMMARY

Several studies have been devoted to the units and mechanisms for emitting VOCs from preliminary and primary treatment. For bar racks and grit chambers, mass balance equations have generally been used to estimate VOC emissions. Mass balance equations have also been used for clarifier surfaces, as well as more sophisticated models such as TOXCHEM+, WATER8, WATER9 and BASTE. At clarifier weirs, the focus has been on measurements of oxygen transfer with the intent of using relationships between oxygen transfer and transfer of VOCs to estimate VOC emissions.

REFERENCES

1. Meyerhofer, J.A., Schroeder, E.D., Corsi, R.L. and Chang, D.P.Y., Control of volatile organic compound emissions during preliminary and primary treatment, *Proc. Water Pollution Control Federation/U.S. EPA Workshop Toxic Air Emissions and POTWs*, Alexandria, Virginia, 1989.
2. Tsivoglou, E.C. and Neal, L.A., Tracer measurement of reaeration: III. Predicting the reaeration capacity of inland streams, *Water Pollut. Contr. Fed. J.*, 48, 2669, 1976.
3. Rahme, Z.G., Zytner, R.G., Corsi, R.L. and Madani-Isfahani, M., Predicting oxygen uptake and VOC emissions at enclosed drop structures, *J. Environ. Eng.,* 47, 1997.

4. Lewis, W.K. and Whitman, W.G., Principles of gas absorption, *Ind. Eng. Chem.,* 16: 1215–1220, 1924.
5. Mackay, D. and Yeun, A., Mass Transfer coefficient correlations for volatilization of organic solutes from water, *Envir. Sci.Tech.*, 17: 211–217, 1983.
6. Springer, C., Lunney, P.D. and Valsaraj, K.T., Emission of hazardous chemicals from surface and near surface impoundments to air, U.S. EPA, Solid and Hazardous Waste Research Division, *Project Number 808161-02*, Cincinnati, Ohio, 1984.
7. MacKay, D. and Matsunaga, R.S., Evaporation rates of liquid hydrocarbon spills on land and water. *J. Chem. Eng.* (Canada), 51: 434–439, 1973.
8. Cohen, Y., Cocchio, W. and Mackay, D., Laboratory study of liquid-phase controlled volatilization rates in presence of wind waves, *Environ. Sci. Technol.*, 12, 553, 1978.
9. O'Connor, D.J., Wind effects on gas-liquid transfer coefficients, *J. Environ. Eng.*, 109: 731, 1983.
10. Dobbs, R.A., Wang, L. and Govind, R., Sorption of toxic organic compounds on wastewater solids: correlation with fundamental properties, *Environ. Sci. Technol.*, 23: 1092, 1989.
11. Pincince, A.B., Transfer of oxygen and emissions of volatile organic compounds at clarifier weirs, *Res. J. Water Pollut. Contr. Fed.*, 63: 114, 1991.
12. Nakasone, H., Study of aeration of weirs and cascades, *J. Environ. Eng.*, 113: 64, 1986.
13. Labocha, M., Oxygen uptake and emissions of volatile Organic compounds at clarifier weirs, thesis, University of Guelph, Ontario, 1994.
14. Matter-Muller, C., Gujer, W. and Giger, W., Transfer of volatile substances from water to the atmosphere, *Water Res.*, 15: 1271, 1981.
15. Rathbun, R.E. and Tai, D.Y., Volatilization of ketones from water. *J. Water Air Soil Pollut.*, 11: 281, 1982.
16. Rathbun, R.E. and Tai, D.Y., Techniques for determining volatilization coefficients of priority pollutants in streams, *Water Res.*, 15: 243, 1981.
17. Mihelcic, J.R., Baillod, C.R., Crittendon, J.C. and Rogers, T.N., Estimation of VOC emissions from wastewater facilities by volatilization and stripping, *J. Air Waste Mgmt. Assoc.*, 43: 97-105, 1993.

8 VOC Emissions from Dissolved Air Flotation

Hugh Monteith and Wayne Parker

CONTENTS

8.1 Introduction 127
8.2 Process Description 127
8.3 Measuring Emissions from DAF Unit 128
8.4 Modeling 129
8.5 Pilot and Field Studies 131
  8.5.1 Pilot Studies 131
  8.5.2 Full-Scale Studies 140
8.6 Summary 142
References 142

8.1 INTRODUCTION

Dissolved air flotation (DAF) is commonly employed at POTWs to separate suspended solids, colloidal matter and wastewater streams. This chapter provides a brief process description of DAF and describes the difficulties associated with measuring its emissions. Various modeling methods used to estimate VOC emissions are presented and results of relevant pilot and field studies are described.

8.2 PROCESS DESCRIPTION

In DAF, a waste stream is pressurized to dissolve excess air and subsequently depressurized to release the air from solution. When the pressure is reduced, the air forms bubbles around wastewater suspended particles, which act as nucleoids. As the bubbles rise to the water surface, the particles are drawn along with them. As the particles accumulate at the surface, a scum or separate phase of oil or solids will form, which is then skimmed off of the flotation tank surface for subsequent processing or disposal. Figure 8.1 presents a process schematic for a typical DAF unit (U.S. EPA).[1]

VOCs may be emitted from DAF units by the release of contaminated bubbles from the flotation tank, volatilization from the float on the surface of the flotation

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

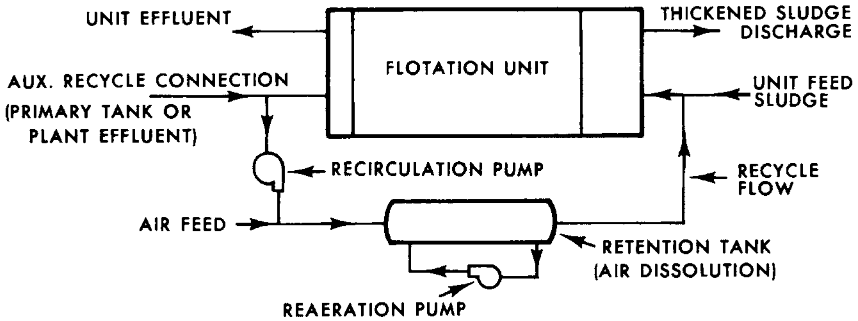


FIGURE 8.1 Schematic of a typical dissolved air flotation unit (U.S. EPA, Process Design Manual for Sludge Treatment and Disposal, *U.S. Environmental Protection Agency Report No. EPA/625/1-77-006,* Office of Technology Transfer, Washington, D.C., 1974).

tank and volatilization from the exposed water on the surface of the flotation tank. Gas phase emissions from the DAF process may be especially significant when located near the head end of a waste treatment train where high concentrations of VOCs are present in the wastewater stream. The petroleum refining industry typically employs DAF in this manner.

The contribution of the previously defined mechanisms to the overall volatilization in the process will depend upon:

- Fractional saturation of the bubbles with VOCs
- Partitioning of VOCs to the float or oil phase
- Impact of the presence of the float on the volatilization of VOCs from the flotation tank surface

8.3 MEASURING EMISSIONS FROM DAF UNITS

DAF processes are nonbiological processes with no degradation mechanisms. Hence, air emissions can be estimated by sampling the inlet, outlet and float streams for the target compounds. This information can be incorporated into a process mass balance with the gaseous emissions determined as the different between the mass flows entering and leaving the process in the liquid streams. However, considerable error in the gaseous emission estimates can result for several reasons. These include:

- Difficulties associated with analyzing VOCs in float streams, especially those with a high proportion of oil
- Variability in inlet and outlet concentrations with time that causes deviations from assumption of steady state for mass balances
- Discontinuous removal of float causing deviation from steady state
- Full-scale studies of VOC emissions from DAFs units have employed floating flux chambers to quantify gaseous emissions.[2]

8.4 MODELING

Parker and Monteith[3] have developed a steady state model based upon the assumption that bubbles generated in the flotation basin of a DAF process are formed at the microscopic level and increase in size with agglomeration and pressure reduction as they rise to the surface of the basin. Hence, the bubbles have a very high surface-to-volume ratio that enhances liquid–gas mass transfer. Therefore, for the purposes of modeling, it is assumed that the gas phase concentration of a VOC, upon exiting the flotation tank, is in equilibrium with respect to the liquid-phase concentration and the compound's Henry's Law coefficient. The rate of stripping due to the bubbles is shown in Equation 8.1:

$$r_s = Q_g C_b H_c \tag{8.1}$$

where

r_s = rate of stripping, mg/h
Q_g = rate of gas flow exiting tank, m^3/h
C_b = liquid concentration of VOC in the flotation basin, μg/L
H_c = Henry's Law coefficient, L liquid/L gas

The offgas flow rate (Q_g) can be estimated from the recycle flow rate, pressure and temperature as defined in Metcalf and Eddy.[4]

In the model, the rate of volatilization from the surface of the flotation basin is defined as shown in Equation 8.2:

$$r_v = K_L A \left(C_b - \frac{C_g}{H_c} \right) \tag{8.2}$$

where

r_v = rate of volatilization, mg/hr
K_L = liquid-gas mass transfer coefficient, m/hr
A = tank surface area, m^2
C_g = gas phase concentration, μg/L
H_c = Henry's Law coefficient

The mass transfer coefficient (K_L) is defined as shown in Equation 8.3:

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{k_g H} \tag{8.3}$$

where

k_l = liquid phase mass transfer coefficient, m/hr
k_g = gas phase mass transfer coefficient, m/hr

The mass transfer coefficients for surface volatilization are estimated using the correlations developed by Mackay and Yeun.[5] This derivation assumes that volatilization from the surface of the DAF is the same as volatilization from clean water. Under normal operation, DAF surfaces are usually partly covered with float and for completeness, mass transfer from the float-covered surface should be addressed separately. However, the fraction of the surface area covered with float usually varies temporally, depending on the mechanism of float removal. Mass transfer through the float, such as an oil film, will likely be less than that through an equivalent water film due to increased viscosity and reduced diffusivities of the contaminants in the oil. Because of the uncertainties associated with the fraction of the surface covered with float, the proposed model addresses only volatilization from an open water surface, as this should provide a maximum estimate of emissions.

The model assumes that partitioning of VOCs to oils can be modeled by the compound's octanol-water partitioning coefficient (K_{ow}). Barbari and King[6] have demonstrated that the partitioning of VOCs to octanol is similar to partitioning to oils. Therefore, the partitioning is modeled as shown in Equation 8.4:

$$q = \frac{K_{ow}}{\rho} C_b \tag{8.4}$$

where

q = mass of contaminant sorbed per mass of oil, μg VOC/mg oil
ρ = density of octanol, mg/L
C_b = concentration of VOC in the waste stream, mg/L

In the following mass balance equations, the term K_{ow}/ρ will be referred to as K_p. The mass balance equation for the liquid phase of the flotation basin assumed a completely mixed flow regime and was therefore defined as shown in Equation 8.5:

$$\begin{aligned} &Q_o\left(1+K_pO_o\right)C_o - Q_1\left(1+K_pO_1\right)C_1 - Q_2\left(1+k_pO_2\right)C_1 \\ &-Q_gC_1H_c - K_LA\left(C_1 - \frac{C_g}{H_c}\right) = 0 \end{aligned} \tag{8.5}$$

where

O_o, O_1, O_2 = oil concentrations in the influent, effluent and float, respectively, mg/L
C_o, C_1 = contaminant concentrations in the influent and effluent, respectively, μg/L
Q_o, Q_1, Q_2 = flow of the influent, effluent and float, respectively, L/hr
Q_1 = $Q_o - Q_2$

Equation 8.5 can also be employed for DAF units being employed for suspended solids removal. In this application, the partitioning coefficient (K_p) is that which describes liquid–solid partitioning for the substance, with the concentrations O_o, O_1, O_2 replaced by X_o, X_1 and X_2, representing the suspended solids concentrations in the influent, effluent and float, respectively.

If the DAF is open to the atmosphere, it can usually be assumed that gas phase concentrations (C_g) are negligible and Equation 8.5 can be solved for C_1. When the DAF under study is covered and vented, a mass balance must also be performed on the headspace gas phase. This equation is defined as shown in Equation 8.6:

$$-Q_{sweep}C_g + Q_g C_1 H_c + K_L A\left(C_1 - \frac{C_g}{H_c}\right) = 0 \tag{8.6}$$

where

Q_{sweep} = flow rate of sweep air through headspace

Equations 8.5 and 8.6 can be solved simultaneously to determine the fate of the VOCs due to adsorption, volatilization and passthrough via the effluent in a DAF.

8.5 PILOT AND FIELD STUDIES

Relatively few studies evaluating VOC emissions from DAFs have been reported. This section reports the results of studies that span from pilot to full scale.

8.5.1 PILOT STUDIES

Parker and Monteith[3] reported testing of a pilot scale unit treating dosed tapwater and wastewater from an oil refinery. Figure 8.2 provides a flow schematic of the pilot DAF unit used in this study. The study objectives were to:

- Measure the emissions of VOCs from a pilot scale DAF unit
- Assess the impact of hydraulic loading and recycle (and hence air to liquid ratio) on the liquid-gas mass transfer of VOCs from DAF units
- Develop and verify models for VOC emissions from DAF units

The study was conducted at an oil refinery that processed western Canada crude to produce gasoline, diesel oil, jet fuel, heating oil and bunker oil. The wastewater stream from the refinery was neutralized with caustic soda to a pH ranging from 9.5 to 9.7 and was conditioned with polymer and allowed to flocculate for a period of 6 to 8 h.

In the DAF pilot plant, the wastewater stream entered directly into the flotation tank, which had a volume of 1.9 m^3 and a surface area of 1.25 m^2 (approx. dimensions 1.5 × 0.83 × 1.5 m deep). A recycle stream was withdrawn from the bottom of the flotation tank and pumped into a pressurization tank. A solenoid controlled valve regulated the air pressure in the tank in the range of 63 to 65 psig. The air pressure was employed to push the recycle stream through a flow controlling valve and into the flotation tank.

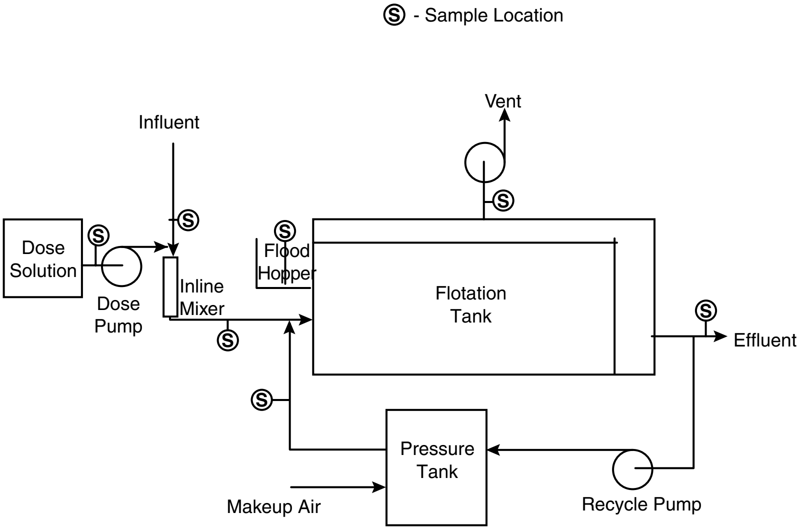


FIGURE 8.2 Pilot DAF flow schematic. Parker, W.J. and Monteith, H.D., Stripping of VOCs from dissolved air flotation, *Environ. Prog.*, 15, 73-81, 1996. With permission.

For the study, the headspace of the DAF tank was essentially sealed from the atmosphere with the headspace volume estimated to be 0.5 m^3. For study purposes, the float was manually removed from the flotation tank surface as required. A vacuum cleaner was employed to withdraw air from the headspace with makeup air pulled from the surrounding ambient air through narrow gaps in the headspace cover. A flow controlling valve and an inline rotameter were employed to fix the venting rate.

In all of the experiments conducted in this study, the influent was dosed with a methanol solution containing a selection of candidate compounds (Table 8.1).

The experiments conducted in this study consisted of three experiments in which tapwater was dosed and eight experiments in which wastewater was dosed with a methanol solution containing selected VOCs. Dosed tapwater experiments were performed to assess the validity of the dosing and sampling procedures and to provide a baseline reference of the behavior of the candidate compounds in the absence of an oily phase. In the dosed tapwater experiments, the pilot plant was operated with an influent flow rate of 4.54 m^3/hr, a recycle flow rate of 4.54 m^3/hr, a recycle pressure of 63 psig and a liquid temperature of 23°C.

The dosed wastewater experiments examined the volatilization from a wastewater matrix that contained oils and suspended solids and also investigated the impacts of hydraulic loading and recycle rate on the fate of the VOCs in the DAF unit. The dosed wastewater experiments are summarized in Table 8.2. The temperature of the pilot plant contents ranged from 29.5 to 33°C over the experimental period. A headspace sweep air flow rate of 8.5 m^3/hr was maintained in each experiment.

In each experiment, liquid phase samples were collected for VOC analysis from the non-dosed wastewater, dosed influent, flotation tank effluent and float streams. Gas phase samples for VOC analysis were collected from the headspace sweep air in every experiment along with occasional sampling of the ambient air.

TABLE 8.1
Properties of Model Compounds

Compound	Vapor Pressure (Torr @ °C)[a]	Solubility (mg/L @ °C)[a]	Henry's Law Coefficient $L_{liq.}/L_{gas}$	Log K_{ow} Partition Coefficient	Aliphatic/Aromatic	Halogenated
Chloroform	160 @ 20	9300 @ 25	0.150[d1]	1.97[a]	Aliphatic	Y
1,1,1-Trichloroethane	100 @ 20	4400 @ 20	0.703[d1]	2.47[a]	Aliphatic	Y
Trichloroethylene	77 @ 25	110 @ 25	0.392[d1]	2.53[a]	Aliphatic	Y
Toluene	28 @ 25	515 @ 20	0.277[d2]	2.69[a]	Aromatic	N
Tetrachloroethylene	19 @ 25	150 @ 25	0.723[d1]	2.53[a]	Aliphatic	Y
o-Xylene	5 @ 20	175 @ 20	0.210[c]	3.12[a]	Aromatic	N
Bromoform	5.6 @ 25	3200 @ 30	0.018[c]	2.30[a]	Aliphatic	Y
1,1,2,2-Tetrachloroethane	4 @ 25	2900 @ 20	0.011[c]	2.56[a]	Aliphatic	Y
1,3,5-Trimethylbenzene	1 @ 9.6	20	0.290[c]	3.42[a]	Aromatic	N
1,4-Dichlorobenzene	1.8 @ 30	79 @ 25	0.137[c]	3.39[a]	Aromatic	Y

[a] U.S. EPA, Autothermal Thermophilic Aerobic Digestion of Municipal Wastewater Sludge, EPA/625/10-90/007, Washington, DC, 1990.

[b] Howard, P.H., *Handbook of Environmental Fate and Exposure Data For Organic Chemicals: Volume II Solvents*, Lewis Publishers, Chelsea, Michigan, 1990.

[c] Ashworth, R.A., Howe, G.B., Mullins, M.E. and Rogers, T.N., Air–water partitioning coefficients of organics in dilute aqueous solutions, *J. Haz. Mat.*, 18, 25–36, 1988.

[d1] Gosset, J.M., Measurement of Henry's Law constants for C1 and C2 chlorinated hydrocarbons, *Environ. Sci. Technol.*, 21, 202–208, 1987.

[d2] Munz, C. and Roberts, P.V., Gas- and liquid-phase mass transfer resistances of organic compounds during mechanical surface aeration, *Water Res.*, 23, 589, 1989.

TABLE 8.2
Summary of Process Conditions for Experiments Conducted with Wastewater

Experiment Order	Temp. (°C)	Liquid Flow Rate (m^3/h)	Recycle Rate (m^3/h)	Recycle Ratio (%)	Calc. Air Release Rate (m^3/h)
1	28.5	2.27	2.27	100	0.172
2	29.0	2.27	1.14	50	0.086
3	28.5	4.54	4.54	100	0.351
4	28.5	4.54	2.27	50	0.172
5	29.5	4.54	2.27	50	0.172
6	29.5	4.54	4.54	100	0.351
7	31.0	2.27	2.27	100	0.172
8	31.5	2.27	1.14	50	0.086

TABLE 8.3
Concentrations Measured in Third Dosed Tapwater Experiment

Compound	Dosed Tapwater (μg/L)	Effluent (μg/L)	Offgas (ng/L)
Bromoform	62.1	62.35	728
1,1,2,2-Tetrachloroethane	71.4	71.75	425
1,4-Dichlorobenzene	82.1	83.15	2540
Toluene	88.2	84.05	4980
o-Xylene	86.8	85.65	4710
1,1,1-Trichloroethane	93.4	88.1	9520
1,3,5-Trimethylbenzene	90.9	91.3	6100
Trichloroethylene	96	93.65	6920
Tetrachloroethylene	98.4	96.35	10700
Chloroform	101	97.2	3980

Consistent behavior was observed in the dosed tapwater experiments. Table 8.3 presents, as an example, the concentrations of the candidate compounds that were measured in the third experiment. Table 8.3 indicates only slight differences between the influent and effluent liquid concentrations. In most cases, the differences were less than the accuracy of the analytical method (approx. 5%). Therefore, only the gas phase measurements were employed in subsequent calculations to estimate the extent of volatilization from the process.

The data collected in the experiments were employed in mass balance analyses to assess the extent of volatilization of the candidate compounds from the DAF.

TABLE 8.4
Volatilization Results from Dosed Tapwater Mass Balance Analyses for Experiment 2

Compound	Volatilization (%)
Chloroform	1.04
1,1,1-Trichloroethane	2.63
Trichloroethylene	1.89
Toluene	1.45
Tetrachloroethylene	2.88
o-Xylene	1.41
1,4-Dichlorobenzene	0.86
Bromoform	0.33
1,1,2,2-Tetrachloroethane	0.18
1,3,5-Trimethylbenzene	1.82

Table 8.4 provides an example of the extent of volatilization of the influent mass, using results from Experiment 2.

Tetrachloroethylene and 1,1,1-trichloroethane were volatilized to the greatest extent in the dosed tapwater experiments, with the percent volatilized ranging from 2.16 to 3.38. 1,1,2,2-Tetrachloroethane was volatilized to the least extent with the percent volatilized ranging from 0.14 to 0.18. The data suggested a strong relationship between percent volatilized and the Henry's Law coefficient of the compounds. Figure 8.3 presents a plot of the average percent volatilized in the tapwater experiments vs. the Henry's Law coefficient. Figure 8.3 indicates that, over the range of Henry's law values that were examined, the relationship is almost linear in nature, with only a slight deviation from linearity as the value of Henry's law coefficient increases. A linear relationship between the percent volatilized and the Henry's law coefficient would suggest that the bubbles exiting the flotation basin were essentially saturated with respect to the Henry's Law coefficient and the liquid concentrations for the compounds tested. Compounds of higher volatility would deviate to a greater extent from this linear relationship, due to an anticipated decrease in the fractional saturation.

Table 8.5 presents the measured concentrations of the candidate compounds in a dosed wastewater, which was conducted with low influent flow rate and a low recycle ratio. These results typify those obtained in the other experiments. In the dosed wastewater experiments, the candidate compounds were added to attain target concentrations of 100 μg/L. However, the measured concentrations of toluene, o-xylene and 1,3,5-trimethylbenzene were all considerably higher than the target concentrations. On average, the concentrations of toluene, o-xylene and 1,3,5-trimethylbenzene in the non-dosed wastewater were 3960, 980 and 190 μg/L, respectively. This observation was not unexpected, since these aromatic hydrocarbons are common constituents of untreated refinery wastewaters. Since there was substantial

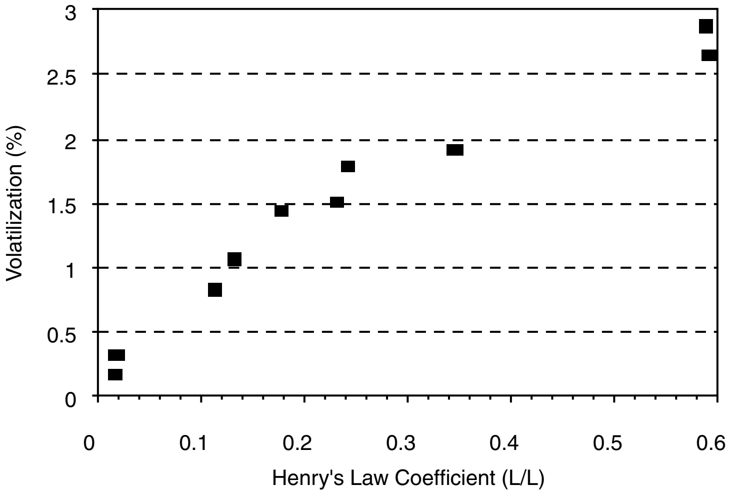


FIGURE 8.3 Percent volatilized vs. Henry's Law coefficient — tapwater experiments. Parker, W.J. and Monteith, H.D., Stripping of VOCs from dissolved air flotation, *Environ. Prog.*, 15, 73-81, 1996. With permission.

TABLE 8.5
Concentrations of Candidate Compounds in Wastewater in Experiment 8

Compound	Background Wastewater (μg/L)	Dosed Wastewater (μg/L)		Effluent (μg/L)		Float (μg/L)	Offgas (ng/L)	
		D1	D2	D1	D2		D1	D2
Chloroform	8.59	110	112	113	111	73.3	313	292
1,1,1-Trichloroethane	17.8	118	121	125	122	72	1790	1790
Trichloroethylene	0.42	107	113	132	126	77.1	1170	1140
Toluene	4000	3800	3650	3720	3280	2400	22300	20800
Tetrachloroethylene	0.86	99.8	105	101	98.1	118	2380	2420
o-Xylene	1000	930	878	935	824	1490	10300	9910
1,4-Dichlorobenzene	0.01	82	86.4	82.3	84	118	884	861
Bromoform	ND	84	86.2	84.8	85	4.87	179	160
1,1,2,2-Tetrachloroethane	ND	78.3	81.8	58.9	58.8	31.1	145	133
1,3,5-Trimethylbenzene	230	142	135	140	119	988	4480	4440

Parker, W.J. and Monteith, H.D., Stripping of VOCs from dissolved air flotation, *Environ. Prog.*, 15, 73-81, 1996. With permission.

variability in the concentrations of these compounds, steady state with respect to time could not be ensured. These compounds were thus eliminated from subsequent mass balance analyses.

An additional process stream, the float from the flotation basin, was analyzed in the dosed wastewater experiments. The float samples were scraped from the surface of the flotation basin upon completion of each experiment and consisted of a mixture of the oily substances present on the flotation basin surface and water entrapped in the float. On average, the concentrations measured in the float were 80% of those observed in the flotation basin effluent. It is suspected that some of the contaminants originally present in the water phase may have preferentially sorbed into the oily phase of these samples during storage. Since the rate of float production was small relative to the wastewater flowrate (<1%), the potential error in analysis of this stream was believed to have minimal influence on the conclusions obtained from the study.

The average percentages volatilized in the replicate experiments for each of the candidate compounds are presented in Table 8.6. It is apparent from Table 8.6 that the compound properties and process operating conditions had a substantial impact on the extent of volatilization measured from the DAF. The extent of volatilization observed in the pilot ranged from 0.19% for 1,1,2,2-tetrachloroethane in the low flow–low recycle scenario to 9.85% for tetrachloroethylene in the same scenario. The impact of wastewater flow rate on the percent volatilized is readily apparent. For virtually all of the compounds, the percent volatilized increased substantially when the wastewater flow rate was decreased. As an example, the volatilization of tetrachloroethylene increased from 5.18% to 8.46% for the high recycle conditions and from 4.26% to 9.85% for the low recycle conditions.

Q = Wastewater Flow Rate; R = Recycle Ratio

An analysis of variance (ANOVA) procedure was employed to statistically assess the impact of wastewater flow rate, recycle ratio and compound type on the stripping of the candidate compounds from the DAF. The procedure indicated that influent flow rate and compound type had a significant effect on the extent of volatilization from the DAF. Effluent recycle did not have a statistically significant effect upon the extent of volatilization. However, the ANOVA procedure also indicated that there were significant interactions between the factors. For all compounds, the extent of volatilization was greater in the high flow-high recycle scenario compared to the high flow-low recycle scenario. A similar trend was not apparent under the low flow conditions.

The air emissions from the DAF likely result from a combination of surface volatilization and stripping to bubbles, which rise through the flotation basin. Given the relatively low removal efficiencies observed in this study, the basin liquid concentrations did not vary substantially amongst experiments. Hence, the rate of surface volatilization was expected to have been relatively constant across the experiments. The observed differences in emissions must therefore have resulted from stripping to the bubbles. Under the conditions of low bubble production (low flow), the impact of varying the recycle rate, which directly influences the rate of bubble production, would be less than that under high flow conditions. Hence, with the variability in the data and the relative increase in importance of surface volatilization relative to stripping, the impact of varying recycle under low flow conditions could likely not be detected under the low flow conditions.

TABLE 8.6
Average Percent Volatilized in Dosed Wastewater Experiments

Compound	Average Percent Volatilized			
	High Q High R	High Q Low R	Low Q High R	Low Q Low R
Chloroform	0.52	0.37	1.01	0.86
1,1,1-Trichloroethane	3.34	2.61	6.30	5.49
Trichloroethylene	2.17	1.60	4.08	3.68
Toluene	1.26	0.90	1.75	2.23
Tetrachloroethylene	5.18	4.26	8.46	9.85
o-Xylene	2.18	1.60	3.21	5.73
1,4-Dichlorobenzene	1.73	1.69	3.20	3.65
Bromoform	0.28	0.22	0.65	0.96
1,1,2,2-Tetrachloroethane	0.40	0.38	0.60	0.19
1,3,5-Trimethylbenzene	5.79	4.96	9.26	9.02

WERF. 1998. Modeling the stripping and volatilization of VOCs in wastewater. Report No. 91-TFT-1, Water Environment Research Foundation, Alexandria, Virginia.

The Parker and Monteith model (1996) was evaluated by comparing estimates of the volatilization of the candidate compounds from the pilot DAF under each of the four operating conditions to the observed data. It should be noted that no calibration was performed with the experimental data to arrive at the emissions estimates.

The estimates are presented vs. the observed values for each of the process operating conditions in Figure 8.4. The results presented in this figure would suggest that, under all conditions of high wastewater flow and also for the condition of low wastewater flow with high recycle, the model was able to adequately predict the emissions of VOCs from the pilot DAF. This is reflected by the generally random distribution and minimal scatter of the residuals about the perfect fit line. Under the conditions of low wastewater flow and low recycle ratio, the model tended to underpredict the emissions as compared with the observed values. Under these conditions, almost all of the compounds demonstrated observed values greater than those predicted by the model.

To further investigate the modeling estimates, the predicted percent volatilized from the DAF was separated into that emitted as a result of air stripping and that emitted by surface volatilization. The values attributed to each mechanism are summarized in Table 8.7. With the exception of bromoform and 1,1,2,2-tetrachloroethane, under high flow and high recycle conditions, the surface volatilization contributed less than 10% of the overall emissions. Under low flow and low recycle conditions, greater than 10% of the emissions, with the exception of tetrachloroethylene and 1,1,1-trichloroethane, resulted from surface volatilization. Four of the seven compounds examined had more than 20% of the emissions resulting from surface volatilization under low flow conditions.

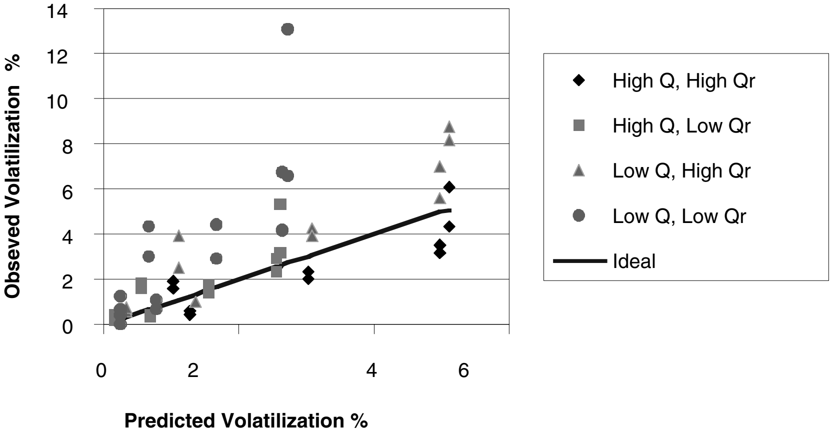


FIGURE 8.4 Comparison of predicted and observed emission rates, pilot DAF unit.

The results would suggest that the error in the model would lie in the surface volatilization component. Under high flow and high recycle conditions, this component is relatively small and errors in this component would not be detectable. Under low flow and recycle conditions, the contribution of surface volatilization is greater relative to the total stripping. Therefore, errors in this component of the model likely mask the effect of changing the recycle flow rate.

Based on the results observed in the pilot plant, it would appear that the surface volatilization model underpredicts the emissions from this source. The underestimation of surface volatilization is inconsistent with the theoretical impact of the presence of an oil layer on the flotation basin surface. Theoretically, the oil layer would tend to reduce emissions, since diffusivities would be lower and turbulence would be reduced in the more viscous liquid. Reduced diffusivities would result in a reduced overall mass transfer of VOCs. In the two-film theory of mass transfer, the lower level of turbulence would result in thicker mass transfer films and, hence, reduced mass transfer. However, the float that tends to accumulate on the surface of oil refinery DAF basins is more of a foam than an oil layer. It may be that the foam acts to increase the effective surface available for mass transfer and that the surface volatilization is greater than would be expected from even an open water surface. It is interesting to note that studies on auto-thermophilic aerobic digesters (ATAD) have demonstrated rates of oxygen mass transfer into digesting sludge greater than those attainable in clean water.[12,13] It has been hypothesized that this increased rate of mass transfer results from mass transfer into the layer of foam typically observed on the surface of ATAD units. Further research is required to quantify this potential mechanism of mass transfer.

Al-Muzaini et al.[14] reported the results of a pilot scale study of VOC stripping from a dosed water stream and from oil refinery wastewater. The study addressed effect of detention time on stripping of VOCs and VOC removal from refinery wastes.

The DAF unit consisted of an air-sealed holding tank from which wastewater was pumped to the DAF flotation tank that had a volume of 0.592 m^3. A recirculation

TABLE 8.7
Volatilization from DAF by Mechanism

	Relative Contribution of Mechanisms (%) to Total Emissions							
	High Q - High R		High Q – Low R		Low Q - High R		Low Q - Low R	
Compound	**Bubble**	**Surf.**	**Bubble**	**Surf.**	**Bubble**	**Surf.**	**Bubble**	**Surf.**
Chloroform	93.2	6.8	88.0	12.0	88.1	11.9	79.0	21.0
1,1,1-Trichloroethane	97.8	2.2	96.2	3.8	96.3	3.7	93.1	6.9
Trichloroethylene	96.7	3.3	94.2	5.8	94.2	5.8	89.3	10.7
Tetrachloroethylene	97.8	2.2	96.4	3.6	96.4	3.6	93.6	6.4
Bromoform	67.9	32.1	51.2	48.8	51.3	48.7	33.8	66.2
1,1,2,2-Tetrachloroethane	60.7	39.3	44.1	55.9	44.2	55.8	28.1	71.9
1,4-Dichlorobenzene	90.8	9.2	83.6	16.4	83.7	16.3	71.8	28.2

WERF. 1998. Modeling the stripping and volatilization of VOCs in wastewater. Report No. 91-TFT-1, Water Environment Research Foundation, Alexandria, Virginia.

stream was pumped through a pressurizing tank to provide the dissolved air. A rotating skimmer was employed to remove the float from the flotation tank.

The experimental program included five phases during which the pilot plant was operated as a continuous flow system at different flow rates and with different streams being treated. The hydraulic retention time was controlled at about 1 hr. The effluent flow was 10 L/min, while the recycle flow was approximately 7.5 L/min. The pressure maintained in the pressurizing tank was 4.5 bars (450 kPa). Tests were conducted at a temperature of 22 ± 2°C. Liquid samples were taken from the influent and effluent points, while air samples were collected from the surrounding area and from the headspace of the DAF unit. The report did not indicate how this information was employed to estimate removal efficiencies.

The major VOCs found in typical refinery wastewater were selected for use as model compounds in the dosed water experiments. These included benzene, toluene, o-xylene and p-xylene, which were dosed into the water to produce an initial concentration of 500 μg/L. The results indicated that VOC removal increased from approximately 4% at an air–water ratio of 0.1 to 19% at an air–water ratio of 0.75. However, substantial removals were observed only when air-to-water ratios greatly exceeded those typically required for oil removal.

Upon completion of dosed water testing, a reconstituted refinery wastewater was treated to evaluate the impact of oil concentration on the removal of VOCs as well as oil and grease. From this testing, it was apparent that, as the oil concentration in the wastewater increased, the removal efficiencies for the model compounds and the oil and grease decreased. Removal efficiencies of the BTEX compounds were typically 22% at an influent oil concentration of 100 mg/L. These removal efficiencies declined to approximately 5% at an influent oil concentration of 500 mg/L. This decrease was attributed to an increase in the quantity of oil floating on the surface of the flotation tank.

TABLE 8.8
Summary of Removal Efficiencies with Refinery Wastewater

Compound	Removal Efficiency (%)
Benzene	18.5
Toluene	25.9
Ethylbenzene	19.0
p-Xylene	18.1
Oil/Grease	55.7

The final group of tests examined VOC and oil and grease removal from an actual wastewater. The results of this testing are summarized in Table 8.8 and show that the removal efficiencies ranged from 14.7% for p-xylene to 37% for toluene.

8.5.2 FULL-SCALE STUDIES

Witherspoon[2] reported field testing of VOC emissions from full-scale DAFs treating oil refinery wastewater. In the field testing, a flux box was floated on the surface of the flotation tank and gas phase emissions were estimated using the California Air Resource Board source test procedure. In this procedure, a sweep air is pulled through the flux box at a measured flow rate. Gas phase concentrations measured in the headspace are employed with sweep air flow rates to estimate a flux of VOCs off the surface. The total emissions from the DAF are determined as the product of the VOC flux and the total surface area of the flotation tank. The reported emissions from the refinery DAFs are summarized in Table 8.9.

Enviromega[15] evaluated the gas phase emissions of a range of VOCs from two DAFs operating at a petrochemical plant and treating storm and process wastes, respectively. Two rounds of testing, each of which involved sampling on two consecutive days, were conducted on each DAF. Gas phase concentrations exiting the surface of the DAF were measured using a floating flux chamber. Emissions were calculated using these concentrations and air flow rates estimated from the recycle flow rate and the pressure employed in the pressurization tank. The average percentage stripped for each of the VOCs is summarized in Table 8.10.

From Table 8.10, it is apparent that, with the exception of a few highly volatile substances, the fraction of VOCs emitted from refinery wastewaters is relatively small (<1%). However, because the concentrations of VOCs in refinery wastewaters is quite high, the concentrations of VOCs in the offgases can be high and present an exposure risk to employees working in the area.

8.6 SUMMARY

The following observations summarize the material reviewed in this chapter:

TABLE 8.9
DAF Emissions Reported by Witherspoon

Refinery	Wastewater Flow (MM gal/d)	Total Hydrocarbon Emissions (lb/d)
Tosco	4.5	124
Shell	4.3	133
Exxon	1.7	67
Unocal	2.2	18

TABLE 8.10
Percentage of VOCs Stripped in Full Scale DAFs (Enviromega)

Compound	Process Waste DAF	Storm Waste DAF
Benzene	0.26	0.17
Cyclohexane	7.97	2.49
Toluene	0.18	0.20
Octane	20.95	n.a.
m,p-Xylene	0.18	0.14
o-xylene	0.14	0.26
Ethylbenezene	0.16	0.16
1,2,4-Trimethylbenzene	0.21	0.11
1,3,5-Trimethylbenzene	0.31	0.44
3-Ethyltoluene	0.18	0.19
2-Ethyltoluene	0.26	0.37
Propylbenzene	0.12	n.a.
1,4-Diethylbenzene	0.25	0.73
1,3-Diethylbenzene	0.19	0.50
Styrene	0.04	0.03

n.a. = not analyzed

- Fractional saturation of the offgas relative to the liquid phase concentrations and Henry's Law is likely for all but highly volatile compounds.
- Results generally indicate that the fraction of influent mass volatilized is slight.
- The model underpredicts under low-Q, low-Qr condition due to underprediction of volatilization.
- VOC removal increases with detention time and air-to-water ratios.
- Almost all information regarding VOC emissions from DAFs is from industrial applications where oil is removed; there is little information from municipal applications where solids would be removed in the float.

REFERENCES

1. U.S. EPA, Process Design Manual for Sludge Treatment and Disposal, *U.S. Environmental Protection Agency Report No. EPA/625/1-77-006,* Office of Technology Transfer, Washington, D.C., 1974.
2. Witherspoon, J.R., VOC and toxic emissions from dissolved air flotation units in the Bay Area, *Proc. 82 Annual Meeting of the Air & Waste Management Association*, June 25–30, Anaheim, California, 1989.
3. Parker, W.J. and Monteith, H.D., Stripping of VOCs from dissolved air flotation, *Environ. Prog.*, 15, 73-81, 1996.
4. Metcalf and Eddy, Inc. *Wastewater Engineering Treatment, Disposal and Reuse*, McGraw-Hill, New York, 1980.
5. Mackay, D. and Yeun, T.K., Mass transfer coefficient correlations for volatilization of organic solutes from water, *Environ. Sci. Technol.*, 17, 211, 1983.
6. Barbari, T.A. and King, C.J., Equilibrium distribution coefficients for extraction of chlorinated hydrocarbons and aromatics from water and undecane, *Environ. Sci. Technol.,* 16, 624, 1982.
7. U.S. EPA, Water Engineering Research Laboratory Treatability Database Version 2.0, U.S. EPA, Cincinnati, Ohio., 1990.
8. Howard, P.H., *Handbook of Environmental Fate and Exposure Data for Organic Chemicals: Volume II Solvents*, Lewis Publishers, Chelsea, Michigan, 1990.
9. Ashworth, R.A., Howe, G.B., Mullins, M.E. and Rogers, T.N., Air–water partitioning coefficients of organics in dilute aqueous solutions, *J. Haz. Mat.*, 18, 25–36, 1988.
10. Gosset, J.M., Measurement of Henry's Law constants for C_1 and C_2 chlorinated hydrocarbons, *Environ. Sci. Technol.*, 21, 202–208, 1987.
11. Munz, C. and Roberts, P.V., Gas- and liquid-phase mass transfer resistances of organic compounds during mechanical surface aeration, *Water Res.*, 23, 589, 1989.
12. U.S. EPA, *Autothermal Thermophilic Aerobic Digestion of Municipal Wastewater Sludge*, EPA/625/10-90/007, Washington, DC, 1990.
13. Wolinski, W.K. and Postings, I. The effect of foam on sewage sludge aeration, *Effluent Water Treat. J.,* 1984.
14. Al-Muzaini, S., Khordagui, H. and Hamouda, M.F., Removal of VOCs from refinery and petrochemical wastewaters using dissolved air flotation, *Water Sci. Technol.*, 30(3) p. 79–90, 1994.
15. Enviromega, Inc. 2000. Internal data.
16. WERF. 1998. Modeling the stripping and volatilization of VOCs in wastewater. Report No. 91-TFT-1, Water Environment Research Foundation, Alexandria, Virginia.

9 VOC Emissions from Biological Treatment Systems: Activated Sludge Process

Prakasam Tata and Cecil Lue-Hing

CONTENTS

9.1 Introduction 145
9.2 Process Description 146
    9.2.1 Activated Sludge Process with Diffused Aeration Using Air 146
    9.2.2 Activated Sludge Process Using High Purity Oxygen Aeration 146
    9.2.3 Mechanical Aeration Processes 146
9.3 Fate of VOCs in Biological Treatment Systems 147
    9.3.1 Volatilization and Stripping 147
    9.3.2 Sorption 148
        9.3.2.1 WATER8 Model 148
        9.3.2.2 TOXCHEM+ Model 149
        9.3.2.3 BASTE Model 151
9.4 Summary 152
References 153

9.1 INTRODUCTION

Activated sludge is by far the most widely used secondary biological treatment process for treating wastewater at many major POTWs. This chapter provides process descriptions for three activated sludge processes: with diffused aeration using air, using high purity oxygen and mechanical aeration. The three phenomena that dictate fate of VOCs in biological treatment systems are also discussed: volatization and stripping, sorption (absorption and adsorption) and biodegradation. A comparison of the three VOC fate models most commonly used to treat these phenomena — WATER8, TOXCHEM+ and BASTE — is then presented.

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

9.2 PROCESS DESCRIPTION

9.2.1 Activated Sludge Process with Diffused Aeration Using Air

In the activated sludge process, effluent from the primary clarifiers is allowed to flow into tanks, where it is aerated either by air or pure oxygen. In some POTWs, primary clarification may not be practiced and raw sewage is aerated in the activated sludge tanks without primary clarification. Aerobic heterotrophic bacteria (microorganisms that utilize oxygen as an electron acceptor and use organic matter for their synthesis and energy requirements) metabolize the dissolved, colloidal and, to some extent, particulate organic material that is biodegradable in the aeration tanks.

During this biological aerobic process, the newly synthesized microorganisms, along with the other inert particulate material, are biologically flocculated. The suspension of this aerated and flocculated material, called mixed liquor, is allowed to settle in secondary settling tanks or final clarifiers. A portion of the settled solids from the secondary settling tanks is returned to the head end of the aeration tanks to mix with the incoming primary effluent, or raw sewage as the case may be, to undergo aeration in the aeration tanks. The portion of the secondary sludge returned to the aeration tanks is called the returned activated sludge (RAS). The remainder, i.e., the portion not returned to the aeration tanks, is wasted from the system and is called the waste activated sludge (WAS, Figure 9.1). A detailed discussion of the activated sludge process and its variations and design considerations can be found in standard references.[1–3]

9.2.2 Activated Sludge Process Using High Purity Oxygen Aeration

In systems using HPO aeration, high purity oxygen (HPO), usually cryogenically generated onsite, is used for aeration instead of the atmospheric air. The same principles of operation that apply to the diffused air aeration activated sludge process also apply to the HPO process. The aeration tanks are covered. HPO is injected through a hollow shaft to a sparging device or injected into the head space of the tank. Surface aerators installed on the shaft of mixers located along the length of the aeration tank bring the HPO into contact with the mixed liquor. Compared with the air activated sludge process, the volume of air required is greatly reduced in the HPO system. Also, the venting rate from the HPO system is considerably lower. Because a very high dissolved oxygen concentration is possible due to the increased oxygen solubility, it is possible to operate the HPO systems at a higher BOD loading and mixed liquor suspended solids (MLSS) concentration than is possible with the conventional air activated sludge systems. The concentration of the MLSS in HPO systems can be in the range of 4,000 to 8,000 mg/L.

9.2.3 Mechanical Aeration Processes

In these processes, aeration is provided by mechanical agitation of the mixed liquor. Mechanical devices such as surface aerators, rotors, brush aerators, jet pumps, etc.

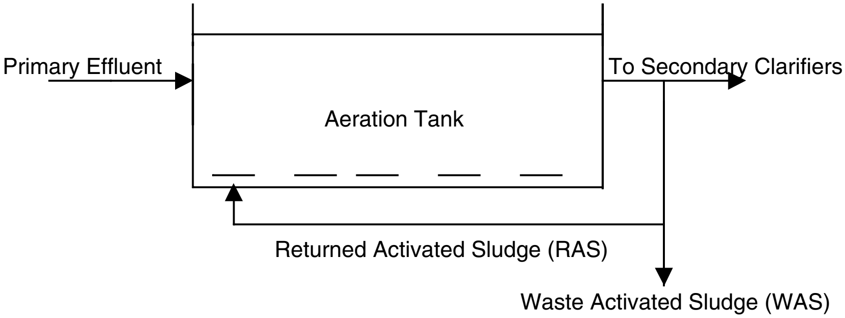


FIGURE 9.1 Activated sludge tank with aeration schematic.

are used. When repeatedly disturbed liquid surfaces come into contact with the ambient air, these devices cause turbulence of the mixed liquor that enables the transfer of oxygen contained in the ambient air.

9.3 FATE OF VOCs IN BIOLOGICAL TREATMENT SYSTEMS

Three main phenomena dictate the fate of VOCs in biological treatment unit processes:

1. Volatilization and stripping
2. Sorption (absorption and adsorption)
3. Biodegradation

These three phenomena have been modeled by various general VOC fate models, among which WATER8, TOXCHEM/+ and BASTE are the most comprehensive and most widely used. A comparison of these, with respect to how the models treat these phenomena, follows.

9.3.1 VOLATILIZATION AND STRIPPING

Volatilization refers to the loss of VOCs from quiescent surfaces, which is primarily driven by the wind blowing at the surfaces. Stripping losses refer to the losses of VOCs from a unit process due to the movement of wastewater. This movement can be caused by mechanical means as in the case of surface aerators and rotors, RBCs, spray nozzles, weir drops or air bubbles moving through a liquid column and then bursting at the surface, as in the case of subsurface aeration devices located in activated sludge tanks. In both the mechanical and subsurface diffused aeration systems, the exposure of the air to the liquid is greatly increased, thus enabling the opportunity for the transfer of VOCs from the liquid phase to the gas phase.

Volatilization and stripping will be the dominant mechanisms for the emission of VOCs from POTW unit processes, where the sorption and biodegradation pathways for VOC fate are absent. Since biological unit processes contain microorganisms that do metabolize and degrade many VOCs, biodegradation plays a significant role in determining the magnitude of VOC emissions from them. Obviously, the fate of those compounds that are either recalcitrant or need a long adaptation period is primarily dictated by volatilization in activated sludge systems, which usually have relatively short solids retention times. Thus, VOC losses by volatilization and stripping decrease correspondingly with increased sorption and biodegradation rates.

The mass transfer rate of a VOC from the liquid to the gas phase and vice versa is a function of its overall mass transfer coefficient. This coefficient is a function of the liquid and gas phase mass transfer coefficients and Henry's law coefficient of the VOCs (Equation 7.7). As long as the VOC concentration is higher in the liquid phase than in the gas phase, volatilization of the VOCs occurs when the surface of the liquid is disturbed by wind currents or by mechanical or subsurface diffused aeration.

9.3.2 SORPTION

Sorption is a physical process that occurs between the particulate material contained in the aeration tank and the VOCs present in solution.

The equations used in the WATER8, TOXCHEM/+ and BASTE models for computation of VOCs by volatilization in aeration systems are given below.

9.3.2.1 WATER8 Model

Subsurface Diffused Aeration (stripping; equilibrium assumed)

$$r_D = Q_g \; H.\ C,/\ RT \tag{9.1}$$

where

r_D = Diffused aeration stripping rate (g/d)
Q_g = Air flow (cu.m/d)
H = Henry's Law constant (atm. m^3/mole)
C = Concentration of VOC in water (g/m^3)
R = Ideal gas constant = 8.206 E-5 (atm. m^3/mole K)
T = Temperature (°K)

Mechanical surface aeration

$$r_M = k_M\, V\, (C - C^*) \tag{9.2}$$

$$1/\, k_M = 1/\, k_{LM} + 1/\, [k_{GM}\, (H/RT)] \tag{9.3}$$

where

r_M = Mechanical stripping rate, (g/d)
k_M = Overall mass transfer coeeficient, (1/d)
V = Tank volume, (m^3)
C = Concentration of VOC in water, (g/m^3)
C^* = Equilibrium concentration of VOC in water, (g/m^3)

k_{LM} = Liquid phase mass transfer coefficient (1/d)
k_{GM} = Gas phase mass transfer coefficient (1/d)
H = Henry's Law constant (atm. m^3/mole)
R = Ideal gas constant = 8.206 E-5 (atm. m^3/mole K)
T = Temperature (°K)

Sorption

$$r_{sorp} = (Q/2)\ X_s \cdot C \cdot (K_{ow})^{0.67}\ (2.455\ E\text{-}6) \quad (9.4)$$

where
r_{sorp} = Sorption rate, (g/d)
Q = Flow into the aeration tank, (m^3/d)
X_s = Organic solids concentration in tank, (g/m^3)
K_{ow} = Octanol-water coefficient
C = Concentration of VOC in water

Biodegradation

$$R_{bio} = k_{max} \cdot X_a \cdot V \cdot C\ /\ (k_{max}/k_1) \quad (9.5)$$

where
R_{bio} = Biodegradation rate, (g/d)
k_{max} = Maximum biorate constant (g/gd)
k_1 = Biodegradation first order rate constant, (g/m^3)
X_s = Organic solids concentration in tank, (g/m^3)
V = Aeration tank volume (m^3)
C = Concentration of VOC in water (g/m^3)

The WATER8 model does not use first order approximation of the Monod relationship in the biodegradation mechanism and therefore requires an additional biodegradation rate constant that must be estimated. The model allows for oil film surfaces in calculations, if present, and also for simulating plug-flow reactors.

9.3.2.2 TOXCHEM+ Model

This model does not assume equilibrium of the VOCs between the liquid and gas phases in the subsurface diffused aeration stripping mechanism. Temperature correction of the Henry's Law coefficient is available in this model. Also, steady state and dynamic conditions can be simulated by this model. The equations used in the model for volatilization, adsorption and biodegradation are given below.

Volatilization — subsurface diffused aeration

$$rD = [Q_g \cdot H \cdot C\ /\ RT]\ [\ 1\text{-exp}\ (\text{-}k_D\ (1/D)V \cdot R \cdot T/H\ Q_g)] \quad (9.6)$$

$$1/k_D = 1/kL_D + 1/kG_D\ (H/RT) \quad (9.7)$$

where
r_D = Diffused aeration stripping rate (g/d)
Q_g = Air flow (cu.m/d)
H = Henry's Law constant (atm. m^3/mole)
C = Concentration of VOC in water (g/m^3)
R = Ideal gas constant = 8.206 E-5 (atm. m^3/mole K)
T = Temperature (°K)
K_D = Overall mass transfer coeeficient, (1/d)
k_{LD} = Liquid phase mass transfer coefficient (1/d)
k_{GD} = Gas phase mass transfer coefficient (1/d)

Volatilization — mechanical surface aeration

$$r_M = k_M (1/D) \cdot V \cdot (C\text{-}C^*) \qquad (9.8)$$

$$1/ k_M = 1/ k_{LM} + 1/ [k_{GM} (H/RT)] \qquad (9.9)$$

where
r_M = Mechanical stripping rate, (g/d)
k_M = Overall mass transfer coefficient, (1/d)
V = Tank volume, (m^3)
C = Concentration of VOC in water, (g/m^3)
C* = Equilibrium concentration of VOC in water, (g/m^3)
k_{LM} = Liquid phase mass transfer coefficient, (1/d)
k_{GM} = Gas phase mass transfer coefficient, (1/d)
D = Depth of aeration tank, (m)

The temperature correction for the Henry's Law constant can be approximated as per the van't Hoff relationship given below.

$$H_t = H_{25}\theta^{(T-25)} \qquad (9.10)$$

where
H_t = Henry's Law constant at T°C
H_{25} = Henry's Law coefficient at 25°C
T = Temperature, °C
θ = Temperature correction factor [1.044]

Sorption

$$q = k_p C \qquad (9.11)$$

where
q = Concentration of contaminant in solid phase, µg/g VSS
k_p = Sorption coefficient, m^3/kg VSS
C = Concentration of VOC in liquid phase, µg/L

The sorption coefficient, $k_{p,}$ can be correlated with the octanol-water coefficient as below,

$$\text{Log } k_p = 0.58 \log k_{ow} = 1.14 \quad (9.12)$$

where

k_{ow} = Octanol-water coefficient

The overall sorption rate can be simulated as follows.

$$r_{sorp} = Q \cdot X_s \cdot C \cdot (K_{ow})^{0.58} \text{ F } (1.38 \text{ E-5}) \quad (9.13)$$

where

r_{sorp} = Sorption rate, (g/d)
Q = Flow rate into aeration tank, (m^3/d)
k_{ow} = Octanol-water coefficient
C = Concentration of VOC in liquid phase, (g/m^3)
F = Biomass fraction = 0.531

From the value of q, obtained in Equation 9.11, one can determine the mass of VOC adsorbed to the solids mass in the aeration tank by the volume of the aeration tank and the concentration of the VSS in the aeration tank.

Biodegradation

Biodegradation losses of VOCs in the aeration tank can be expressed by the following equation.

$$r_{bio} = k_1 \cdot X_a \cdot V \cdot C \quad (9.14)$$

where

r_{bio} = Biodegradation rate, (g/d)
k_1 = First order biodegradation rate constant (m^3/g.d)
X_a = Biomass concentration, (g/m^3)
V = Volume of the aeration tank, (m^3)
C = Concentration of VOC in water (g/m^3)

9.3.2.3 BASTE Model

Volatilization, adsorption and biodegradation of VOCs are modeled in the BASTE model as per the following equations.

Volatilization — Subsurface Diffused Aeration

$$r_d = [Q_g \cdot H \cdot C \cdot /R \cdot T]\,[1\text{-exp}(-k_{LD} \cdot V \cdot R \cdot T \cdot /HQ_g)] \quad (9.15)$$

where

r_d = Diffused stripping rate, (g/d)

Q_g = Air flow, (m^3/d)
H = Henry's Law constant, (atm. m^3/mole)
C = Concentration of VOC in water (g/m^3)
R = Ideal gas constant = 8.206 E-5 (atm. m^3/mole K)
T = Temperature, K
K_{LD} = Liquid phase mass transfer coefficient, (1/d)
V = Aeration tank volume, (m^3)

Volatilization — Mechanical Surface Aeration (Stripping)

BASTE model simulates volatilization by stripping in mechanical surface aeration systems using the same equations used in the WATER8 model. However, the BASTE model has the ability to correct the Henry's Law constant to the prevailing temperature of the wastewater.

Sorption

Sorption in the aeration systems is modeled as follows with the BASTE model.

$$r_{sorp} = Q \cdot X \cdot C \cdot k_{ow} F (6.3 \text{ E-7}) \qquad (9.16)$$

where

r_{sorp} = Sorption rate (g/d)
Q = Flow into aeration tank, (m^3/d)
X = Organic solids concentration, (g/m^3)
k_{ow} = Octanol-water coefficient
C = Concentration of VOC in water (g/m^3)
F = Biomass fraction = 0.531

Biodegradation

Biodegradation is simulated by the BASTE model using following equation.

$$r_{bio} = k_1 \cdot X_a \cdot V \cdot C \qquad (9.17)$$

r_{bio} = Biodegradation rate, (g/d)
k_1 = Biodegradation first-order rate constant, (m^3/d)
X_a = Biomass concentration, (g/m^3)
V = Aeration tank volume, (m^3)
C = Concentration of VOC in water, (g/m^3)

9.4 SUMMARY

A comparison of these general fate models with respect to VOC emissions from the activated sludge aeration basins is presented in Chapter 14. In general, all the above fate models overpredict VOC emissions from the aeration basins of POTWs. When predicted VOC emission rates are below "major source" definition values (i.e., 10 tons of a specific VOC per year or 25 tons of total VOCs per year), a POTW manager can be reasonably assured that the actual VOC emission rates obtained by direct measurements by the flux chamber technique described in Chapter 12 would be far below the predicted VOC emission rate. It is prudent to determine the annual VOC emission rate by direct measurement; if the model-predicted VOC emission rates are found to be higher than the major source definition VOC emission rate. Emission rates determined by direct measurements in such instances would likely be below the major source emission rate value.

The results of various studies, presented in Chapter 14, indicate that VOC emission rates predicted by the BASTE and TOXCHEM+ models are generally significantly lower than the emission rates predicted by the WATER8 model. Hence, it is recommended that a plant manager use the BASTE or TOXCHEM+ models for estimating VOC emission rates from POTWs, if required, particularly when such computed emission rates are found to be below the major source threshold values. A municipal agency should get approval from state agencies for the use of these models if it is necessary to submit VOC emission rates for any regulatory purpose.

REFERENCES

1. Metcalf and Eddy, Inc., *Waste Water Engineering: Treatment, Disposal, Reuse*, McGraw-Hill, New York, 2003.
2. Fair, G.M. and Geyer, J.C., *Water Supply and Wastewater Disposal,* John Wiley & Sons, New York, 1961.
3. Veismann, W., Jr. and Hammer, M.J., *Water Supply and Pollution Control,* Addison Wesley, Menlo Park, C., 1998.

10 VOC Emissions from Fixed Film Processes

Hugh Monteith and Wayne Parker

CONTENTS

10.1 Introduction 155
10.2 Process Descriptions 155
  10.2.1 Trickling Filters 155
  10.2.2 Rotating Biological Contactors 156
10.3 Modeling 156
  10.3.1 Trickling Filters 156
  10.3.2 Rotating Biological Contactor Studies 161
  10.3.3 Pilot Scale Studies 163
10.4 Summary 170
References 170

10.1 INTRODUCTION

Wastewater treatment processes that incorporate carriers for support of biofilms are commonly referred to as fixed film processes and include trickling filters (TFs), rotating biological contactors (RBCs), biological aerated filters (BAFs) and other hybrid processes. Relatively little information is available to describe the emissions of VOCs from fixed film processes. This chapter describes work that has been conducted to assess VOC emissions from RBCs and TFs.

10.2 PROCESS DESCRIPTIONS

10.2.1 TRICKLING FILTERS

In TFs, wastewater is uniformly dosed over a packed rock or plastic media and allowed to trickle downward through it. Mass transport processes move the substrate to and through the biofilm attached to the media. Oxygen is transferred from the air-filled void spaces to the wastewater through gas–liquid mass transfer as the wastewater trickles over the media or packing. Gas movement in the TF is most often due to natural convection induced by temperature differences between the air

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

and the wastewater. Occasionally, TFs are force ventilated by pulling air through the spaces of the packed media with a fan. An effluent recycle is often employed to increase wetting frequency during low flow periods and to enhance biomass sloughing. A typical process schematic for a TF process is presented in Figure 10.1.

10.2.2 ROTATING BIOLOGICAL CONTACTORS

RBCs consist of partially submerged circular disks that rotate within a basin that contains wastewater. Oxygen is transferred to the film of wastewater drawn out of the basin on the rotating disks. Substrate moves into the biofilm that grows on the disks where biodegradation occurs. Some biodegradation may result from suspended growth of biomass in the basin, but this is normally assumed to be negligible. Figure 10.2 presents a typical RBC process schematic.

10.3 MODELING

10.3.1 TRICKLING FILTERS

Parker et al.[1] derived a steady state model for the fate of VOCs in TFs based on the following assumptions:

- Steady state with respect to time
- Counter-current air and wastewater flows with plug flow characteristics
- Negligible background gas phase VOC concentrations
- Stagnant liquid layer between the bulk liquid and biofilm creating an external mass transfer resistance

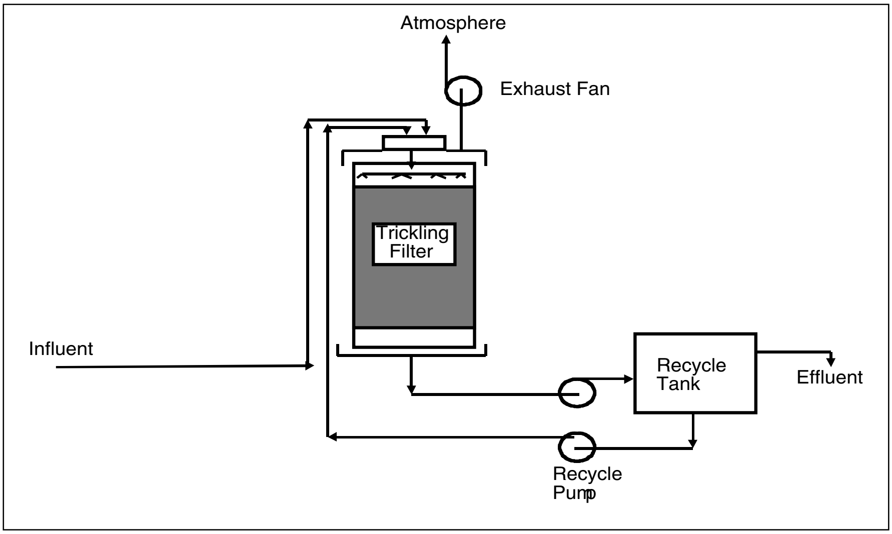


FIGURE 10.1 TF process schematic.

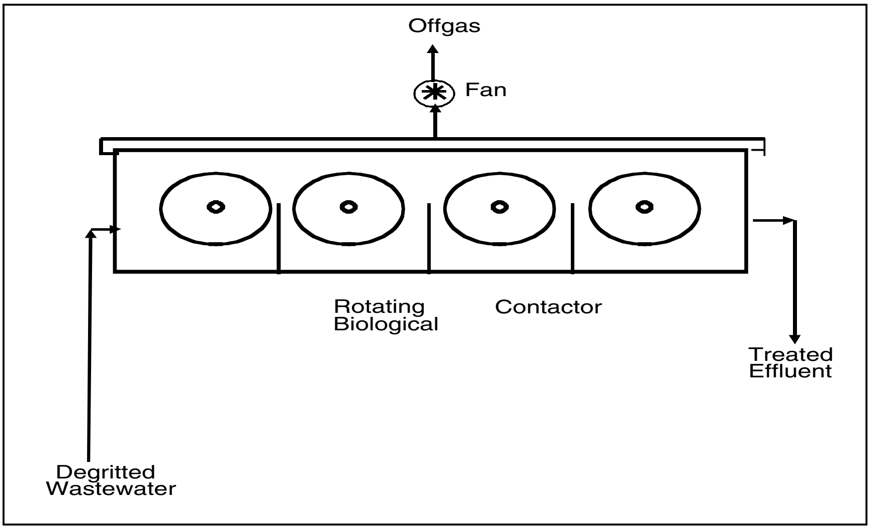


FIGURE 10.2 RBC process flowsheet.

- First-order biodegradation rate with respect to biomass and VOC concentrations
- Internal diffusional resistance through the biofilm
- Constant thickness and density of biofilm for the entire process

Figure 10.3 presents a conceptual schematic of the competing fate pathways for VOCs in the biofilm process model. Symbols presented in Figure 10.3 are defined in the following equations below.

The removal of a VOC in a biofilm was assumed to be by secondary substrate utilization; thus, the removal rate by biodegradation could be described by the expression shown in Equation 10.1:

$$r_b = K_B X_f C \tag{10.1}$$

where:

r_b = rate of biodegradation
K_B = first-order biorate coefficient
C = VOC substrate concentration

At steady state, diffusion and biodegradation in the biofilm is given as shown in Equation 10.2:

$$D_e\left(\frac{\partial^2 C}{\partial z^2}\right) = K_B X_f C \tag{10.2}$$

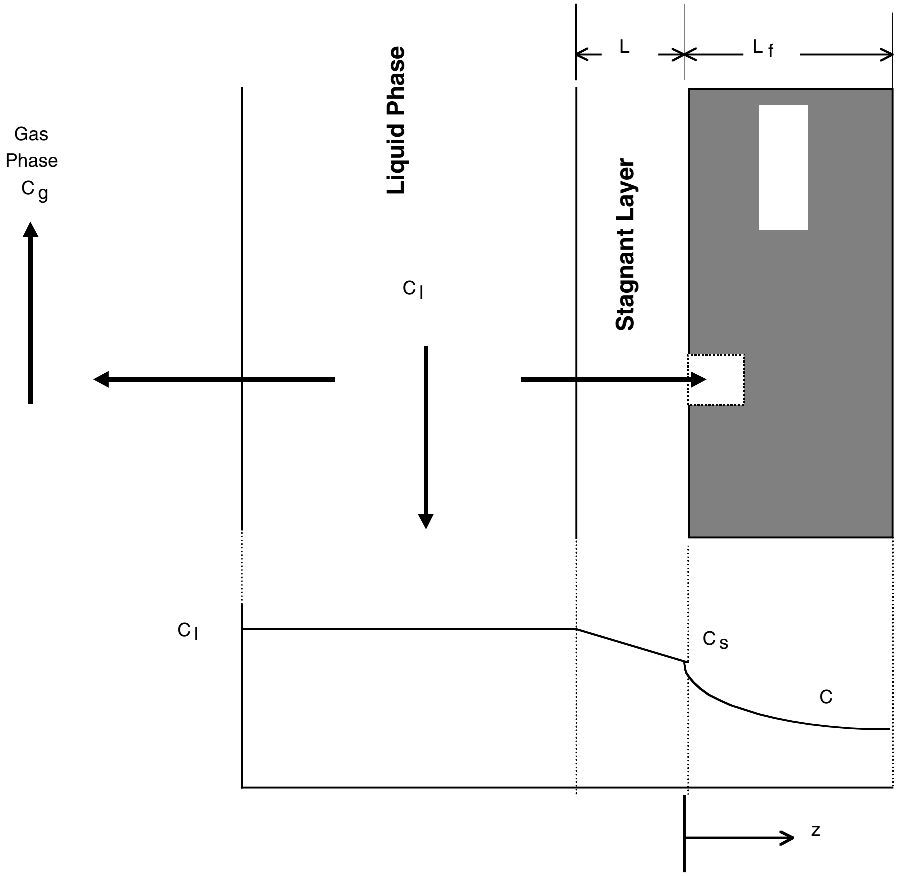


FIGURE 10.3 Conceptual schematic of biofilm.Parker W.J., Monteith, H.D. and Melcer, H., Volatile organic compounds in trickling filters and rotating biological contactors: Part I – pilot studies, *ASCE J. Environ. Eng*, 122, 557, 1996a. With permission.

where:

D_e = diffusivity of VOC in biofilm.

In a biofilm, the boundary conditions assumed to exist are that $C = C_s$ at $z = 0$ and $dC/dz = 0$ at $z = L_f$,

where:

C_s = VOC concentration at outer edge of biofilm

z = distance in biofilm measured from liquid interface

L_f = biofilm thickness

The solution of the above equation, using the prescribed boundary conditions, is then given as:

$$C = C_s \left\{ \frac{\cosh\left[r_1\left(L_f - z\right)\right]}{\cosh\left(r_1 L_f\right)} \right\} \tag{10.3}$$

where

$$r_l = \sqrt{\left(X_f K_B / D_e\right)} \tag{10.4}$$

The mass flux of a VOC at the interface of the biofilm and stagnant layer is given by:

$$N = D_e \frac{dC}{dz} \tag{10.5}$$

Differentiating Equation 10.3 and substituting in Equation 10.5 yields:

$$N = D_e r_1 \tanh(r_1 L_f C_s) \tag{10.6}$$

The mass flux through the stagnant layer (i.e., the external resistance) is equal to the mass flux into the biomass, so that

$$D_e r_1 \tanh(r_1 L_f) C_s = K_L(C_l - C_s) \tag{10.7}$$

The external mass transfer coefficient has been approximated by the expression:[2]

$$K_L = \frac{D}{L} \tag{10.8}$$

Now, Equation 10.7 can be solved for C_s and the resulting equation can be substituted into:

$$N_b = K_L(C_l - C_s) \tag{10.9}$$

to yield:

$$N_b = K_L \frac{D_e r_1 \tanh\left(r_1 L_f\right)}{D_e r_1 \tanh\left(r_1 L_f\right) + K_L} C_l \tag{10.10}$$

Equation 10.10 relates the mass flux into the biofilm to the bulk liquid phase concentration and does not require an iterative solution. Two conditions are of particular interest; when K_L is large, the equation reduces to:

$$N_b = D_e r_1 \tanh(r_1 L_f) C_l \tag{10.11}$$

and when K_L is small, it reduces to:

$$N_b = K_L C_l \tag{10.12}$$

A liquid phase mass balance for a horizontal differential slice of the reactor yields:

$$Q_l dC_l = -(N_v + N_b) a A_x dX \tag{10.13}$$

A gas phase mass balance around the same horizontal differential slice yields:

$$Q_g dC_{\mathrm{g}} = -N_v a A_x dx \tag{10.14}$$

The mass transfer flux due to volatilization is defined as:

$$N_v = K_v \left(C_1 - \frac{C_g}{H_c} \right) \tag{10.15}$$

The mass transfer flux due to biodegradation is defined by Equation 10.10. Simultaneous solution of Equations 10.13 and 10.14, following substitution for N_v and N_b, yields the distribution of gas and liquid VOC concentrations through the depth of the filter.

Parker[3] conducted a multiparameter sensitivity analysis of the model using a frequency array approach. The objective of the study was to identify the ranges of parameters over which model predictions of biodegradation, volatilization and overall removal were particularly sensitive. The model was found to be most sensitive to liquid loading rates less than 20 m^3/m^2day and gas loading rates less than 200 m^3/m^2day. Model predictions were most sensitive to biofilm thickness less than 1×10^{-4} m, liquid–gas mass transfer coefficients less than 0.10 m/day, Henry's Law coefficients less than 0.10 and biodegradation rate coefficients less than 20 m^3/kg-day. When employing the model for predictive purposes, greater care should be taken in defining parameters for compounds that lie in this range.

Ockeloen et al.[4] employed a similar approach to model the removal of VOCs in a gas stream by biological treatment in a TF. A general model of substrate flux to a biofilm, provided by Rittman and McCarty,[5] was used by Ockeloen et al.[4] as the basis for the TF. The flux model used by Ockeloen et al. was given by:

$$N = \sqrt{2 D_F K_s \hat{q} X_f} \sqrt{\frac{C_L}{K_s} - \ln\left[1 + \frac{C_L}{K_s}\right]} \tag{10.16}$$

where:

D_f = molecular diffusivity of the substrate in the biofilm

K_s = Monod half-saturation constant
$\hat{q}$ = maximum specific substrate utilization rate
X_f = biomass density

Both co-current and counter-current air flow regimes were considered. The mass balance for the gas phase in the TF was given by:

$$\frac{dC_G}{dh} = -\frac{K_L a}{u_G}\left(C_L^* - C_L\right) \tag{10.17}$$

The liquid phase balance for counter-current flow was given as:

$$\frac{dC_L}{dh} = -\frac{K_L a}{u_L}\left(C_L^* - C_L\right) + \frac{N}{u_L} \tag{10.18}$$

Or, for co-current flow, as:

$$\frac{dC_L}{dh} = -\frac{K_L a}{u_L}\left(C_L^* - C_L\right) - \frac{N}{u_L} \tag{10.19}$$

where:
C_G = gas phase substrate concentration
C_L = liquid phase substrate concentration
C_L* = liquid phase substrate concentration in equilibrium with gas phase (= S_G/ H_c)
h = trickling filter height
$K_L a$ = overall mass transfer coefficient
u_L = superficial liquid velocity
u_G = superficial gas velocity
H_c = Henry's law coefficient
N = substrate flux into the biofilm.

The simulations considered the case with recycle of the liquid stream back to the TF, so that the liquid concentrations at the bottom and top of the filter were equal (i.e., C_L (h = 0) = C_L (h = h_{max})).

The differential equations were solved numerically to yield the simulation results. The simulations showed that, as Henry's law coefficient (H_c) increases, i.e., as solubility decreases, the removal efficiency of the bioscrubbing process decreased. The first step in VOC removal is the transfer of the compound from the gas phase to the water film overlying the biofilm. Sparingly soluble compounds do not transfer readily to the liquid phase. Co-current air direction was found to be superior to counter-current flow for removing compounds with higher values of H_c, while, at lower values of H_c, both flow regimes removed the VOCs efficiently. Biological removal of the contaminants in the gas phase increased with the height of the trickling filter.

10.3.2 ROTATING BIOLOGICAL CONTACTOR STUDIES

Hao et al.[6] considered the potential of the RBC process as a stripper of VOCs from contaminated water. Modeling equations were developed in the absence of a biofilm such that stripping was the only removal mechanism. The model assembled by Hao et al. considered the RBC to consist of a completely mixed process for the basin connected to a plug flow reactor that describes the liquid conveyed out of the basin by the disks of the RBC. Through standard mass balances and mass transfer equations, the authors were able to show that the liquid phase concentration at any stage of a RBC process can be estimated by the expression:

$$C_n = C_o \frac{1}{\left(1 + \left[\frac{V}{nQ}\right] K_{app}\right)^n} \tag{10.20}$$

where:

C_n = substrate concentration exiting stage n of the RBC
C_o = influent substrate concentration
V = liquid volume within the RBC model boundary
n = number of stages of the RBC
K_{app} = overall mass transfer parameter for the VOC substrate

The value of K_{app} is a function of the operating conditions including disk dimensions, number of disks, degree of submergence and disk surface area:

$$K_{app} = \left(K_2 + \frac{\left(R^2 - R_i^2\right)}{V_2} \frac{4 n_d f}{15} \sqrt{\frac{2 \nu R \sin\phi}{g}} \varpi^{1.5} \right) \tag{10.21}$$

where:

K_2 = liquid-gas mass transfer coefficient for mixed basin
R = radius of disk
R_I = radius on non-submerged disk
V_2 = volume of mixed basin
n_d = number of disks in basin
f = disk surface area correction factor
ν = kinematic viscosity of water
g = gravitational constant
ϕ = $\cos^{-1}(R_i/R)$

While the RBC model does not describe all of the processes active in an RBC, it does indicate the functionality that should exist between VOC stripping and some process operating parameters.

Parker et al.[1] developed a model for VOC fate in an RBC based on the following assumptions:

- The model is steady state with respect to time.
- Each section of the wastewater basin is a continuous stirred tank reactor (CSTR).
- The headspace of the entire RBC is connected and considered as one CSTR.
- The background gas phase concentrations of the VOCs are negligible.

The mass balance equation for the liquid phase of each basin was therefore:

$$Q_o\left(C_{b_{i-1}} - C_{b_i}\right) - N_{v_i} - N_{b_i} = 0 \tag{10.22}$$

The mass flux due to volatilization from each basin is described as:

$$N_{v_i} = K_v A_e\left(C_{b_i} - \frac{C_g}{H_c}\right) \tag{10.23}$$

The relationship defining mass flux due to biodegradation has been defined in Equation 10.10. The surface area over which this mass flux occurs is assumed to be the total area of the discs that is present in the RBC section. The mass balance on the RBC headspace was therefore defined as:

$$-Q_g C_g + \sum_{i=1}^{N} N_{v_i} = 0 \tag{10.24}$$

10.3.3 PILOT SCALE STUDIES

Hannah et al.[7] reported the results of pilot scale testing of a variety of wastewater treatment processes, including a high-rate TF and a conventional activated sludge process. Influent and effluent concentrations only were reported; hence, the fraction of the VOCs lost to volatilization is unknown. The TF employed in the study was 0.91 m in diameter, 2.4 m high and filled to a depth of 1.9 m with crushed slag media. The removal efficiencies observed in the TF process and the activated sludge process are reported in Table 10.1, from which it can be seen that the removal efficiencies observed in the TF process were substantially lower for all compounds as compared with the activated sludge process. It must, however, be noted that the TF pilot plant employed in this study was relatively shallow in depth, which would tend to minimize the extent of stripping that might occur in a TF. In addition, the media employed in the pilot plant is not commonly employed in modern TFs.

TABLE 10.1
Removal Efficiencies

	High Rate Experiment (1986)		Standard Rate Experiment (1988)	
Compound	Activated Sludge	TF	Activated Sludge	TF
Carbon tetrachloride	74	59	81	90
1,1-Dichloroethane	94	34	97	92
1,1-Dichloroethylene	92	58	>97	>97
Chloroform	86	25	98	89
1,2-Dichloroethane	84	33	95	87
Bromoform	65	57	68	82
Ethylbenzene	93	71	>98	>98

Source: Hannah et al.[7,8]

In a follow-up study,[8] the TF was converted to standard operation and the fate of VOCs was again evaluated. The results of the study are also presented in Table 10.1. From Table 10.1, it can be seen that the standard rate operation removal efficiencies of the VOCs improved substantially over high-rate operation. Under the lower loading rates associated with standard operation, it is likely that the removal of VOCs by stripping and biodegradation would have been enhanced.

Monteith et al.[9] reported on a comparative study of emissions from three fixed film pilot processes (TF, RBC and BAF) operating in parallel. The processes were being assessed as potential candidate processes for upgrading of a chemically enhanced primary treatment plant in Windsor, Ontario. The monitoring study was passive in nature, measuring emissions from the operation without any perturbation of the system or change in influent concentrations. Consequently, many of the targeted list of contaminants were beneath the method detection limits. The results of the study are summarized in Table 10.2. Of the compounds that could be detected, the data suggested that the TF had lower emission rates than the RBC or BAF processes. Mass balances calculated around the processes suggested that biodegradation might have contributed more as a removal mechanism in the TF than in the other two processes, as the air emission mass of the various VOCs is considerably lower in the TF than in the other systems.

Parker et al.[10] reported the results of a controlled series of pilot-scale tests conducted to measure the stripping of VOCs in TFs and RBCs. The TF pilot plant was a 3.66 m deep tower of 22 m^3 volume, equipped with PVC cross-flow media with a specific surface area of 138 m^2/m^3, suitable for producing a nitrified effluent. Municipal wastewater dosed with the candidate compounds was pumped continuously to a distribution box at the top of the filter structure. A siphon inside the distribution box, which simulated intermittent dosing of wastewater to the TF, discharged to a collection trough fitted with perforated channels that distributed liquid over the medium surface. The top of the TF was sealed and a draft was induced up through the TF with an exhaust fan to allow estimation of gas phase mass fluxes from the TF. In the TF experiments, the impacts of wastewater flow rate and implementation of recycle on VOC fate were evaluated.

TABLE 10.2
Emissions from Pilot Fixed Film Wastewater Treatment Units, Windsor, Ontario

	RBC			TF			BAF		
Compound	**Inf. Mass mg/d**	**Air Mass mg/d**	**% of infl.**	**Inf. Mass mg/d**	**Air Mass mg/d**	**% of infl.**	**Inf. Mass mg/d**	**Air Mass mg/d**	**% of infl.**
Chloroform	95.76	215.42	224.96	326.61	130.97	40.10	51.3	44.352	86.46
Benzene	5.6	11.87	212.01	19.1	3.79	19.87	3	2.36	78.54
Trichloroethylene	36.96	31.82	86.10	126.06	17.75	14.08	19.8	5.09	25.70
Toluene	36.4	35.86	98.53	124.15	68.67	55.31	19.5	38.21	195.97
m&p-Xylene	213.92	189.72	88.69	729.62	282.74	38.75	114.6	106.72	93.13
Ethyl benzene	28	22.40	80.00	95.5	40.27	42.17	15	16.47	109.82
o-Xylene	283.92	140.76	49.58	968.37	257.04	26.54	152.1	106.13	69.78

Source: Monteith, H.D., Bell, J.P., Harvey, R.T. and Melcer, H., Investigation of the fate of volatile organic compounds in fixed film wastewater treatment systems. Paper no. 92-94.06, presented at 85th Annual Meeting & Exhibition, Air and Waste Management Assoc., Kansas City, MO, June 21-26, 1992.

The RBC test apparatus consisted of a four-stage Autotrol RBC equipped with 2.0 m-diameter polyethylene discs, providing a total surface area of 734 m^2 that was equally distributed between the stages and covered to seal it from the atmosphere. The RBC basin volume was maintained at 3.45 m^3 for all experiments. This resulted in a disc submergence of 0.68 m and a wetted surface area of approximately 540 m^2. The RBC headspace was vented at a constant flow to allow for estimation of removals due to stripping. In the RBC experiments, the impacts of wastewater flow rate and disk rotational speed on VOC fate were evaluated.

The results of the testing are summarized in Tables 10.3 and 10.4 for the TF and RBC, respectively. The impact of varying the previously described process operating parameters was evaluated using an ANOVA procedure. Increasing the hydraulic loading to the TF resulted in an increased fraction of the VOCs in the effluent. Imposing effluent recycle, in addition to elevating the hydraulic loading, enhanced this effect. However, imposing effluent recycle also resulted in an increase in the biodegraded fraction and decreased the fraction stripped from the TF for more than half of the VOCs. It was expected that, with the reduced HRT resulting from the increased hydraulic loading, the fraction detected in the effluent would have increased and, therefore, reduced removals due to biodegradation and stripping. Imposing recycle would cause the system to deviate hydraulically from plug flow to a backmixed regime.

If first-order removal kinetics are assumed, the change in flow regimes would tend to reduce the system efficiency and result in a higher fraction in the effluent and a lower level of stripping. This behavior was confirmed by the experimental data. If the change in hydraulics from plug flow to mixed regimes was the only mechanism responsible for the behavior of the VOCs, it would be expected that the fraction biodegraded would also decrease. In contrast, however, biodegradation was observed to increase with recycle. It was proposed that this occurred as a result of the increased wetting of the medium surface since effluent recycle is commonly employed in TFs to promote biomass viability through increasing the frequency of wetting the biofilm.

The ANOVA procedure revealed that increasing the hydraulic loading to the RBC increased the fraction of most of the compounds in the RBC effluent and in the offgas streams and reduced the extent of biodegradation of the candidate compounds. Increasing the disc rotational speed was, for most of the compounds, found to increase the biodegraded fraction and decrease the fractions present in the effluent and offgas streams. The impact of disc rotational speed on the fate of the candidate compounds was unexpected, as increased rotational speed would increase the opportunity for liquid–gas mass transfer and tend to enhance the contribution of volatilization. It is apparent that the reduced fractions of the candidate compounds in the effluent and offgas streams at the increased rotational speed resulted from the enhanced contribution of biodegradation.

A differentiation in behavior of the VOCs was proposed based on the dominant removal mechanisms observed in Tables 10.3 and 10.4. The behavior of the VOCs can be described as either highly biodegraded, volatile poorly biodegraded, nonvolatile poorly biodegraded or mixed. The highly biodegraded VOCs included toluene, o-xylene and 1,3,5-trimethylbenzene and typically were present in the effluent and offgas streams at very low concentrations. Tetrachloroethylene is an example of a compound that was poorly biodegraded and volatile. It was detected at low effluent concentrations, with most being detected in the offgas. An example of a poorly degraded but nonvolatile VOC is 1,1,2,2-tetrachloroethane, primarily found in the effluent with low concentrations detected in the offgas. 1,4-Dichlorobenzene is an example of a VOC that demonstrated mixed behavior since there was no dominant removal mechanism.

As previously demonstrated, the process operating parameters influenced the fate of the VOCs in the pilot studies. Direct comparisons of the fates of the compounds between the two processes could, therefore, not be easily performed because the reactors were of different dimensions and were treating different wastewater flows. However, the operating conditions employed for each pilot plant spanned the range of values that would normally be employed in practice. Therefore, the performance of the processes was compared by examining the response ranges for the individual compounds. If a particular process dominated the high end of the range for a response and was less prevalent at the low end, then it was concluded that the process tended to favor that response over the other process.

TABLE 10.3
Fate of VOCs in Trickling Filter

	Low Flow-Recycle			High Flow-Recycle			Low Flow-No Recycle			High Flow-No Recycle			Low Flow-Recycle		
Compound	**% Vol**	**% Eff**	**% Bio**	**% Vol**	**% Eff**	**% Bio**	**% Vol**	**% Eff**	**% Bio**	**% Vol**	**% Eff**	**% Bio**	**% Vol**	**% Eff**	**% Bio**
Chloroform	39.9	19.2	40.8	24.9	32.9	42.2	52.3	8.9	38.8	63.8	20.4	15.8	29.1	23.0	47.9
1,1,1-Trichloroethane	35.4	8.9	55.7	25.1	16.4	58.4	40.2	3.2	56.6	78.2	7.1	14.7	36.0	8.9	55.1
Trichloroethylene	25.1	11.8	63.1	34.1	20.7	45.2	62.1	5.1	32.7	76.0	10.6	13.4	43.6	13.2	43.1
Toluene	6.2	2.2	91.6	7.1	9.7	83.2	17.2	2.0	80.8	22.0	2.8	75.2	7.3	2.0	90.7
Tetrachloroethylene	62.2	9.6	28.3	52.3	17.0	30.7	81.0	2.9	16.1	82.9	7.2	9.9	56.0	9.3	34.7
o-Xylene	18.1	6.0	75.9	10.2	18.7	71.1	19.2	2.6	78.2	22.6	4.0	73.4	10.2	2.2	87.6
1,4-Dichlorobenzene	24.4	19.7	55.9	13.6	36.3	50.1	28.6	8.0	63.4	29.7	14.8	55.4	17.4	13.7	68.9
Bromoform	16.5	26.7	56.8	11.7	49.8	38.5	36.4	28.8	34.8	29.6	52.5	17.9	27.0	67.4	5.6
1,1,2,2-Tetrachloroethane	23.1	63.7	13.3	13.3	78.2	8.5	35.6	55.9	8.5	28.3	77.7	–6.0	22.3	80.1	–2.4
1,3,5-Trimethylbenzene	19.8	8.0	72.2	12.1	19.0	68.9	23.7	2.6	73.7	30.0	4.0	66.0	12.6	2.8	84.7

% Vol = Percent of influent mass flow removed by volatilization

% Eff = Percent of influent mass flow detected in effluent

% Bio = Percent of influent mass flow estimated to be biodegraded

Source: Parker W.J., Monteith, H.D. and Melcer, H., Volatile organic compounds in trickling filters and rotating biological contactors: part I - pilot studies, *ASCE J. Environ. Eng.*, 122, 557, 1996a.

TABLE 10.4
Fate of VOCs in RBC

	Low Flow High Rotation			High Flow High Rotation			Low Flow Low Rotation			High Flow Low Rotation			Low Flow High Rotation		
Compound	**% Vol**	**% Eff**	**% Bio**	**% Vol**	**% Eff**	**% Bio**	**% Vol**	**% Eff**	**% Bio**	**% Vol**	**% Eff**	**% Bio**	**% Vol**	**% Eff**	**% Bio**
Chloroform	24.1	19.7	56.2	20.1	49.6	30.3	40.1	33.8	26.1	43.2	58.9	–2.1	22.9	28.4	48.7
1,1,1-Trichloroethane	25.1	9.7	65.2	32.0	24.8	43.2	38.9	17.5	43.6	63.2	35.9	0.9	36.8	14.7	48.5
Trichloroethylene	24.6	12.2	63.3	43.1	33.1	23.8	46.5	21.0	32.5	62.9	41.8	–4.7	44.9	21.2	33.9
Toluene	13.0	2.4	84.6	13.1	9.3	77.5	14.1	5.2	80.7	23.7	21.3	55.0	10.5	1.4	88.0
Tetrachloroethylene	42.2	8.2	49.6	53.8	22.5	23.7	72.8	14.7	12.6	75.2	32.3	–7.5	50.0	12.9	37.0
o-Xylene	16.5	3.8	79.7	17.9	14.0	68.1	15.3	6.6	78.1	31.3	27.0	41.8	6.9	1.1	92.0
1,4-Dichlorobenzene	31.9	25.8	42.3	21.2	37.2	41.6	30.8	25.3	44.0	31.7	51.9	16.4	13.1	6.2	80.7
Bromoform	5.0	15.5	79.5	4.1	33.3	62.6	8.8	22.8	68.4	6.3	35.6	58.1	6.2	38.0	55.8
1,1,2,2-Tetrachloroethane	13.1	61.3	25.6	8.5	88.3	3.2	22.1	89.5	–11.7	12.7	97.1	–9.8	12.7	82.9	4.4
1,3,5-Trimethylbenzene	21.5	3.1	75.4	22.4	14.8	62.7	22.1	7.4	70.4	41.6	45.3	13.1	11.4	1.5	87.1

Source: Parker W.J., Monteith, H.D. and Melcer, H., Volatile organic compounds in trickling filters and rotating biological contactors: Part I — pilot studies, *ASCE J. Environ. Eng*., 122, 557, 1996a.

The TF tended to have greater losses due to volatilization than the RBC. The RBC consistently dominated the low end of volatilization losses, while the TF had a majority of the high-end volatilization losses. The RBC consistently maintained a greater fraction of the candidate compounds in the process effluent. All of the high-end values for this response were occupied by the RBC, while a majority of the low-end values were occupied by the TF. No discernible trends could be observed for the biodegraded fraction. In fact, the RBC occupied almost all of the high- and low-end values for biodegradation of the candidate VOCs.

Parker et al.[1] calibrated the previously described models for TFs and RBCs using the data from the pilot plant testing. Tetrachloroethylene demonstrated the highest volatilization coefficients, while bromoform and 1,1,2,2-tetrachloroethane demonstrated the lowest values. Toluene, o-xylene and 1,3,5-trimethylbenzene displayed the highest biodegradation rate coefficients, while 1,1,2,2-tetrachloroethane had the lowest values for this parameter. The RBC volatilization rate coefficients were consistently greater than the TF values. It was not possible to conclusively differentiate between biodegradation rate coefficients for the two processes. The TF biodegradation and volatilization coefficients were generally constant over time and were consistent over the range of conditions evaluated in the pilot plant experiments. The RBC results suggested that the rate of biodegradation in RBCs is related to the system organic loading and rate of reaeration. Conditions that tended to promote a depressed dissolved oxygen concentration demonstrated lower biodegradation rate coefficients.

Analysis of the biofilm model revealed that, in the TF, the biofilm was fully penetrated and the external mass transfer did not limit the rate of biodegradation. In the RBC, the modeling indicated that, with the exception of toluene, o-xylene and 1,3,5-trimethylbenzene, diffusion did not limit biodegradation of the candidate compounds and the biofilm was essentially penetrated by the candidate compounds. For the former compounds, diffusion in the biofilm appeared to limit biodegradation.

Analysis of the liquid–gas mass transfer coefficients yielded a ratio between the gas and liquid phase mass transfer coefficients of 91.4 for the TF and 5.6 for the RBC. However, due to the relatively wide confidence intervals associated with these estimates, the values could not be statistically differentiated. Nevertheless, the results did suggest a significant contribution of the gas phase resistance to the overall mass transfer in some cases of the TF operation.

10.4 SUMMARY

Pilot studies have shown that TFs tend to result in higher emission rates than RBCs. For certain compounds under certain operating conditions, gas phase resistance may contribute significantly to overall mass transfer. Models for stripping alone and those combined with biodegradation have been developed for the TF and RBC processes. From the models derived from pilot studies, it was determined that biodegradation in the TF was not limited by diffusion in the biofilm; with the RBC, biodegradation of some aromatic compounds was limited by diffusion in the bioflim. The rate of biodegradation in the RBC was higher than in the TF and was related to the system organic loading and rate of reaeration, which could adversely affect dissolved oxygen levels.

REFERENCES

1. Parker, W.J., Monteith, H.D. and Melcer H. Volatile organic compounds in trickling filters and rotating biological contactors: part II - model studies, *ASCE J. Environ. Eng*., 122, 564, 1996b.
2. Williamson and McCarty, P.L. A model of substrate utilization by bacterial films, *J. Water Pollut. Contr. Fed*., 48, 9, 1976.
3. Parker, W.J. A multi-parameter sensitivity analysis of a model describing the fate of volatile organic compounds in trickling filters, *J. Air Waste Mgmnt. Assoc*., 47, 871, 1997.
4. Ockeloen, H.F., Overcamp, T.J. and Grady, C.P.L., Jr. A biological fixed-film simulation model for the removal of volatile organic air pollutants. Paper no. 92-116.05, presented at 85th Annual Meeting & Exhibition, Air and Waste Management Association, Kansas City, Missouri, June 21–26, 1992.
5. Rittman, B.E. and McCarty, P.L. Variable-order model of bacterial-film kinetics, *J. Environ. Eng. Div. ASCE*, 104 (5), 889, 1978.
6. Hao, O.J., Davis, A.P., Wu, Y.C. and Hsueh, K.P. Modeling volatile organic compound stripping
7. Hannah S.A., Austern, B.M., Eralp, A.E. and Wise R.H., Comparative removal of toxic pollutants by six wastewater treatment processes, *J. Water Pollut. Contr. Fed*., 58 (1), 27, 1986.
8. Hannah S.A., Austern, B.M., Eralp, A.E. and Dobbs R.A., Removal of toxic pollutants by trickling filter and activated sludge,*J. Water Pollut. Contr. Fed*., 60 (7), 1281, 1988.
9. Monteith, H.D., Bell, J.P., Harvey, R.T. and Melcer, H., Investigation of the fate of volatile organic compounds in fixed film wastewater treatment systems. Paper no. 92-94.06, presented at 85th Annual Meeting & Exhibition, Air and Waste Management Assoc., Kansas City, MO, June 21–26, 1992.
10. Parker W.J., Monteith, H.D. and Melcer, H., Volatile organic compounds in trickling filters and rotating biological contactors: Part I – pilot studies, *ASCE J. Environ. Eng*, 122, 557, 1996a.

11 VOC Emissions from Biosolids′ Dewatering Processes

Hugh Monteith and Wayne Parker

CONTENTS

11.1 Introduction 171
11.2 Process Descriptions 171
11.3 VOC Transfer in Dewatering Processes 172
11.4 VOC Transfer Studies 174
11.5 Summary 186
References 187

11.1 INTRODUCTION

Residual solids from wastewater treatment processes are often dewatered prior to disposal on land or in landfills or before further processing (drying, pelletizing, composting, incineration). During dewatering, any volatile compounds present may be stripped or volatilized from the solids. In many cases, the dewatering processes are covered, with headspace air exhausted to foul air collection systems for odor control. In other situations, the process units may be placed in enclosed buildings equipped with exhaust systems, again as an odor control measure in the buildings. In either case, the continuous replacement of process headspace air with "clean" air leads to the maximum driving force for volatilization of organic compounds from the solids. This chapter discusses biosolids dewatering processes most widely used at POTWs and describes VOC transfer in the dewatering process. VOC transfer studies are also reviewed.

11.2 PROCESS DESCRIPTIONS

The processes primarily considered here include belt filter presses, centrifuges and drying beds. Other processes such as vacuum filters or plate-and-frame filter presses

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

are not discussed in detail because of lack of VOC emission data and because they are not in wide use at wastewater treatment facilities.

The operation of belt filter presses and centrifuges usually involves use of organic polymers or inorganic conditioning agents. Schematic representations of a belt filter press and a centrifuge are found in Figures 11.1 and 11.2, respectively. In the filter press, an inclined belt carrying the solids rises from the conditioning tank, allowing water to drain freely by gravity. Spools or paddles are used to distribute the solids evenly on the belt prior to arrival at the low-pressure dewatering zone.

With respect to centrifuges, discussion will focus on the solid bowl (decanter) machine, due to declining use of basket-type centrifuges in municipal biosolids dewatering applications. The decanter centrifuge consists of a cylindrical bowl, tapered at one end, with an inserted helical screw, also called a scroll. Both the bowl and scroll are operated at high rotational speeds, with the scroll speed being slightly different from the bowl speed. The conditioned solids are introduced into the bowl through a pipe. The high rotational speed creates a gravitational force hundreds or thousands of times that of the gravitational constant. This force creates a pool of sludge in which the solids separate from the liquid. The liquid fraction (centrate), containing smaller and unflocculated solids, passes around or through the scroll to a discharge point. The thickened solids are directed by the scroll up the tapered end of the bowl (the beach) to a different discharge point.

11.3 VOC TRANSFER IN DEWATERING PROCESSES

The presence of VOCs in solids for dewatering can be influenced by a number of factors, including:

- Solids concentrations
- Property of each organic compound including volatility, biodegradability and sorptive or hydrophobic properties
- Nature of any industrial inputs
- The type of processes preceding the dewatering process

For example, aerobic biological processes are effective in removing many non-halogenated organics,[1,2] while anaerobic processes are effective in dechlorinating other compounds.[3] While many studies have focused on removal of the parent substrate, processes may result in formation of intermediate metabolites that are also VOCs. For example, in anaerobic conditions, tetrachloroethylene can be sequentially transformed to trichloroethylene, dichloroethylene and vinyl chloride.[4] High levels of toluene in certain digested sludges may also be an indication of its presence as an intermediate metabolite,[5,6] although its elevated concentration as a result of industrial discharges has been suggested.[7]

The underlying mechanisms of VOC transfer in the dewatering devices have been neither well studied nor documented. Surface volatilization is probably the main transfer mechanism in dewatering processes. In belt filter presses, VOCs can be volatilized from the solids in the free drainage and cake discharge areas. VOCs in the filtrate can transfer from the droplets of water squeezed from the solids and

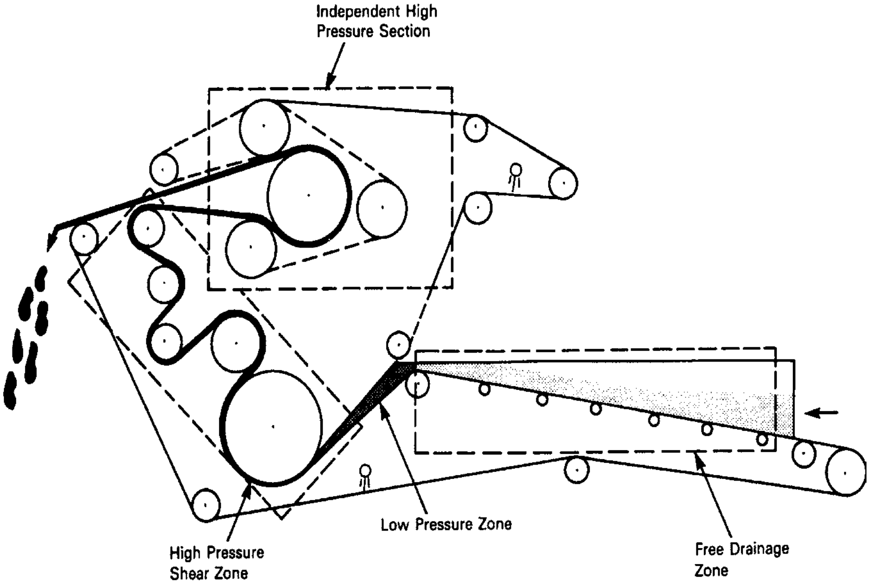


FIGURE 11.1 Schematic of a representative belt filter press.

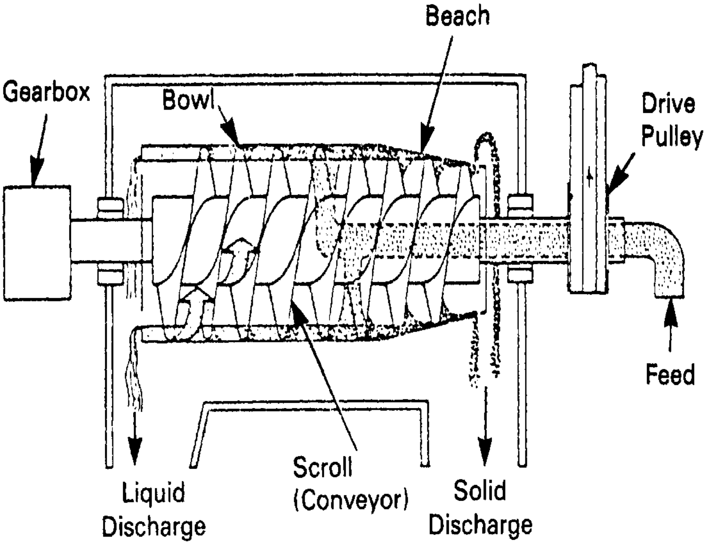


FIGURE 11.2 Schematic of a representative solid bowl centrifuge.

falling through the belts. Washwater may be free of most VOCs initially, but accumulation of the sludge fines in the washwater may provide an opportunity for transfer of any VOCs associated with the fines to the gas phase. In centrifuges, the opportunities for VOC transfer occur as the sludge is discharged to the bowl as a falling film, from shear as the sludge stream contacts the rotating bowl and by volatilization from the cake that forms on the bowl surface. VOCs may also volatilize from the surface of the centrate, particularly as it is discharged and falls by gravity from the centrifuge to the collection pipe or sump. When biosolids are dewatered by drying beds, the transfer mechanism is solely desorption of the VOCs from the surface of the drying beds. In warm climates with constant winds, mass transfer could be substantial.

11.4 VOC TRANSFER STUDIES

The magnitude of VOC emissions from processes that dewater biosolids have not been well documented. The PEEP study for a consortium of California POTWs derived emission factors for 17 specific organic compounds emitted from wastewater processes.[8] Many processes treating liquid and solid streams were investigated. The processes involved in dewatering biosolids were the belt filter press, centrifuge and air drying bed. Derivation of the emission factors was dependent on whether the processes were: (1) covered (thereby permitting collection of a gas phase sample), (2) open surfaces, where covered surface flux chambers could be used to generate a gas phase stream for sampling, or (3) other types of nonbiological processes in which the mass emitted was determined to be the difference between mass loads in and out of the liquid streams. The emissions from the processes were calculated by the expression shown in Equation 11.1:

$$MA = ML^{*}EF \tag{11.1}$$

where

MA = mass of contaminant to air
ML = mass loading of contaminant to the process
EF = calculated emission factor for contaminant in process

The median values of emission factors for biosolids dewatering processes calculated from measured concentrations are reported in Table 11.1. For the remaining compounds of the PEEP study, for which no emission factor could be calculated, an extrapolation procedure was used by J.M. Montgomery to estimate the additional emission factors. Based on their general behavior in biological treatment, the procedure classified the compounds of interest as either nonhalogenated or halogenated. The median of measured emission factors for compounds within the two classes was used to derive the "extrapolated" factors. The compounds and extrapolated emission factors are also reported in Table 11.1.

A report published by the American Petroleum Institute (API[9]) noted some measured VOCs from dewatering processes. For processes without any type of emission control devices, total VOC emissions were approximately 16.1 lb/h. The mass emitted could not be related to the input mass to the dewatering device because of the manner of reporting the data. Reported temperatures ranged from 80 to 200°F, enhancing the emission rates.

TABLE 11.1
Measured Emission Factors for Biosolids Dewatering Devices from PEEP Study

Compound	Median Emission Factor		
	Belt Filter Press	Centrifuge	Drying Beds
Benzene	0.27	0.011	4.5
Carbon tetrachloride	0	0.01	0
Chloroform	0	0.01	0
Dichlorobenzene	0	0.01	0
1,4-Dioxane	0.27	0.023	4.5
Ethylene dibromide	0	0.01	0
Ethylene dichloride	0	0.01	0
Methylene chloride	0	0.01	0
Tetrachloroethylene	0	0.01	0
Styrene	0.27	0.023	4.5
1,1,1-Trichloroethane	0	0.01	0
Trichloroethylene	0	0.01	0
Trichlorofluoromethane	0	0.01	0
Toluene	0.45	0.21	5.2
Vinyl chloride	0	0.01	0
Vinylidene chloride	0	0.01	0
Xylenes	0.098	0.023	4.5
Formaldehyde	0.0092	0.00027	0.076

Ponder and Bishop[10] presented emission factors from belt filter presses at three petroleum refineries. At one, designated Sun-Toledo, the filter presses treated wastes from two different processes, including API separators and DAF. At least two of the sites preheat the feed sludges to a temperature of 130 to 140°F, which will enhance emission rates. The emission factors are provided in Table 11.2. Emission factors for the Sun-Tulsa refinery press were generally higher than for the units at the other two sites. Very high emission factors were obtained for some of the aliphatic hydrocarbons, such as hexane, heptane and methylcyclohexane.

Concentrations of VOCs in the exhaust air from a building housing a centrifuge were reported by Caballero and Griffith.[11] Toluene and xylenes were present at the highest concentrations, up to 625 μg/L, as shown in Table 11.3. Lauria[12] tested the inlet gas to a scrubber from a dewatering device. While the more common VOCs were not detected or present at very low concentrations, formaldehyde was measured at 55,300 μg/L.

Monteith and Bell[5] investigated and modeled VOC emissions resulting from operation of a belt filter press and a centrifuge at municipal POTWs. The study was limited to investigation of only one unit of each type of process. The filter press was equipped with 2.0 m belts with a nominal processing capacity of 600 kg dry solids per hour. Polymer was added at a rate of approximately 5 kg/tonne D.S. Anaerobically digested biosolids were pumped to the belt filter press in batches, two to three times weekly. The duration of each batch treatment was approximately 4 hours.

TABLE 11.2
Emission Factors from Belt Filter Presses Treating Refinery Sludges

Compound	Sun – Toledo API sludge	Sun – Toledo DAF sludge	BP-Lima	Sun – Tulsa
Xylenes	nd	nd	0.046	0.19
1,2,3-trimethylbenzene	NT	NT	0.015	0.071
Ethylbenzene	0.17	0.14	0.061	NT
Methylcyclohexane	0.28	0.23	0.21	0.78
n-Heptane	0.32	0.28	0.31	0.92
n-Hexane	NT	NT	NT	1.3
Toluene	0.25	0.17	0.12	0.39
Benzene	0.38	nd	021	0.26
Ethyltoluene	0.061	0.059	0.024	0073
Naphthalene	0.044	0.5	0.0024	0.018
2-Methylnaphthalene	NT	NT	0.00057	0.0087
Fluorene	NT	NT	.000005	0.00057
Phenanthrene	NT	NT	nd	0.00017
1,3,5-Trimethylbenzene	0.12	0.16	NT	NT

nd = not detected
NT = not tested

TABLE 11.3
Concentrations of VOCs in Air Exhausted from Dewatering Processes

Compound	VOC Concentration (μg/L) in Air from Centrifuge (Caballero and Griffith, 1989)	VOC Concentration (μg/L) in Air from Dewatering Device (Lauria, 1989)
Dichloromethane	<0.5	NR
Trichloromethane	<0.5	NR
1,1,1-Trichloroethane	<0.5	Nd
Trichloroethylene	24	NR
Tetrachloroethylene	70	Nd
Chloroethylene	0.5	NR
Benzene	35	Nd
Toluene	500	15
Xylenes	625	NR
Formaldehyde	NR	55,300

NR = not reported
Nd = not detected

The filter press was contained in a small hemispherical metal building. The press was enclosed from floor to ceiling with clear flexible plastic sheeting for odor containment. A ceiling fan that exhausted air to the building exterior was located directly above the press. During the study, the doors to the dewatering building were closed and the overhead exhaust fan turned off.

For determination of mass balances around the filter press, samples of feed biosolids, filtrate, filter washwater, filter cake and a sweep air sample from the enclosed belt press were collected. To obtain a sample of the belt filter feed sample without added polymer, the bypass from the digester to the drying beds was sampled. Both filtrate and belt washwater samples were collected from the discharge conduit located at the base of the press using a stainless steel cup. Samples of sludge cake were retrieved from a dump truck close to the cake discharge point, used for removal of the dewatered solids. The air and solids temperatures were 26°C

A low volume sweep air through the enclosed filter press was induced by fixing the suction end of a vacuum cleaner hose over the top of the filter press belts. The volumetric flow rate was controlled using a rotameter set at 8.5 L/s (18 cfm). Air samples were collected in stainless steel canisters placed on the walkway over the belts of the press on which the polymer-conditioned sludge was distributed. Two rounds of samples were collected.

Because no flow meter was located in the solids dewatering process, the solids and flow balances were of necessity calculated from solids concentration data and the measured mass of dewatered cake removed from the plant on the day of sampling. This was determined from the tipping fee tickets charged to the plant at the landfill site.

The flow balance was constructed according to Equation 11.2:

$$Q_{si} + Q_{pol} + Q_{ww} = Q_{fil} + Q_{cak} + Q_{ww} \tag{11.2}$$

where

Qsi = feed sludge flow
Q_{pol} = polymer feed flow
Q_{ww} = wash water flow
Q_{fil} = filtrate (or centrate) flow
Q_{cak} = cake flow

The solids mass balance was then constructed as shown in Equation 11.3:

$$Q_{si}X_{si} + Q_{pol}X_{pol} = Q_{fil}X_{fil} + Q_{cak}X_{cak} + Q_{ww}X_{ww} \tag{11.3}$$

where

X_{si} = feed sludge solids concentration
X_{pol} = polymer concentration
X_{cak} = cake solids concentration
X_{fil} = filtrate (or centrate) solids concentration
X_{ww} = wash water solids concentration

The wet cake mass was the only measured mass flow. Solids concentrations were measured in all streams but the added polymer. The observed concentrations and calculated flows for the process streams entering and leaving the filter press are summarized in Table 11.4. With this estimate, the estimated solids capture in the cake was 85%. Calculation of this solids capture was required for estimation of the VOC mass balance closures.

TABLE 11.4
Ingersoll Filter Press Process Stream Characterization

Stream	Flow (L/h)	Solids (g/L)
Feed	17,495	36.17
Wash water	13,620	4.3
Polymer	558	5
Filtrate	15,533	2.4
Cake	2,520	213

Monteith, H.D. and Bell, J.P., Modeling of VOC emissions from biosolids dewatering processes, *Proc. WEFTEC '98, Vol. 6. Facility Operations I & II.* 71st Annual Conference and Exposition, Water Environment Federation, Orlando, FL, October 3–7, 157–168, 1998. With permission

Samples for VOC analysis were collected in replicate runs. Mean values of VOCs in the process streams are presented in Table 11.5. Concentrations in the feed sludge, filtrate and washwater are expressed in µg/L, while concentrations in the sludge cake and sweep air are expressed in ng/g and ng/L, respectively. The concentrations of VOCs in the filtrate and washwater were much reduced compared with the feed sludge levels. More VOCs were detected in the air samples than the liquid samples due to greater sensitivity of the air analysis. Toluene was the predominant compound in the sludge streams, followed by 1,2,4-trimethylbenzene. More non-chlorinated compounds than chlorinated compounds were detected, leading to speculation that the chlorinated compounds were subject to processes such as reductive dechlorination and that the remaining compounds are either recalcitrant to the dechlorination process or are the metabolic intermediates of the process, or both.

The mass balance for VOCs around the filter press was expressed as shown in Equation 11.4:

$$Q_{si}C_{si} = Q_{fil}C_{fil} + Q_{cak}C_{cak} + Q_{ww}C_{ww} + Q_G C_G \tag{11.4}$$

where

Q_G = sweep air flow rate
C_{si} = feed sludge VOC concentration
C_{fil} = filtrate (or centrate) VOC concentration
C_{ww} = wash water VOC concentration
C_{cak} = sludge cake VOC concentration

TABLE 11.5
Mean Concentrations of Representative VOCs in Filter Press Process Streams

Contaminant	Feed ng/L	Filtrate ng/L	Wash water ng/L	Cake ng/g	Air ng/L
Dichloromethane	3.16	1.01	0	37.1	8.5
Toluene	138	14.65	5.59	1915	196
m,p-Xylene	6.68	0.695	0.36	65.4	23.75
3-Ethyltoluene	32.5	1.455	0.835	305	21.75
1,3,5-Trimethylbenzene	18.9	0.795	0.49	166	16.25
1,2,4-Trimethylbenzene	54.5	2.535	1.52	476.5	47.65
1,4-Dichlorobenzene	34.9	1.915	0.945	292	22.75

Monteith, H.D. and Bell, J.P., Modeling of VOC emissions from biosolids dewatering processes, *Proc. WEFTEC '98, Vol. 6. Facility Operations I & II.* 71st Annual Conference and Exposition, Water Environment Federation, Orlando, FL, October 3–7, 157–168, 1998. With permission

C_G = sweep air (or foul air) VOC concentration

The mass balances of representative VOCs around the filter press are provided in Table 11.6. The mean recovery of all compounds was 143%, suggesting either that the mass of VOCs in the feed was underestimated, or that concentrations in the output streams were overestimated. Although there were a number of probable causes for the elevated closures, the most likely source of error was believed to result from the method used to estimate the flows around the filter press.

TABLE 11.6
Mass Balance of Representative VOCs around the Ingersoll Filter Press

Contaminant	Feed (g/h)	Filtrate (g/h)	Wash Water (g/h)	Cake (g/h)	Air (g/h)	Total Out (g/h)	Recovery (Percent of feed)
Dichloromethane	0.055	0.015	0.000	0.097	0.0003	0.113	204.1
Toluene	2.409	0.219	0.076	5.019	0.0060	5.320	220.9
m,p-Xylene	0.117	0.010	0.005	0.171	0.0007	0.187	160.7
3-Ethyltoluene	0.567	0.022	0.011	0.799	0.0007	0.833	146.9
1,3,5-Trimethylbenzene	0.330	0.012	0.007	0.435	0.0005	0.454	137.7
1,2,4-Trimethylbenzene	0.951	0.038	0.021	1.249	0.0015	1.309	137.6
1,4-Dichlorobenzene	0.609	0.029	0.013	0.765	0.0007	0.808	132.6

Monteith, H.D. and Bell, J.P., Modeling of VOC emissions from biosolids dewatering processes, *Proc. WEFTEC '98, Vol. 6. Facility Operations I & II.* 71st Annual Conference and Exposition, Water Environment Federation, Orlando, FL, October 3–7, 157–168, 1998. With permission

The distribution of these representative VOCs in the process streams leaving the filter press is summarized in Table 11.7. Data were presented as a percentage of the sum of the outputs, rather than as a percentage of the input mass, to avoid uncertainties in the influent mass determination. The majority of the VOCs are found in the sludge cake (82 to 99%) and almost none is found in the headspace air over the press (e.g., 0.08 to 0.44%). Slightly greater amounts of the VOCs are found in the filtrate than in the washwater. For the most part, the mass of specific VOCs in filtrate and washwater were together less than 10% of the total output for each compound.

Monteith and Bell[5] also reported on a study of emissions from a full-scale centrifuge at the Highland Creek (Toronto) POTW, a conventional activated sludge facility treating an average daily flow of 175,000 m^3/d. Most of the WAS is co-thickened with primary clarifier solids, with the balance thickened by DAF without polymer usage. Sludge from the primary clarifiers and thickened WAS is blended prior to thermal treatment. The heat-treated solids are dewatered by centrifuge (both Humboldt and Sharples), with the cake solids incinerated as ultimate disposal. Operation of the centrifuges is continuous, but not all centrifuges operate concurrently.

The centrifuge tested was a Sharples centrifuge, processing 840 kg dry solids per hour. The polymer addition rate was 11.78 kg per tonne of dry solids. The dewatered cake was conveyed to an incinerator for final disposal. Centrate from the process was returned to the head of the facility's primary clarifiers. All centrifuges at the Highland Creek POTW are covered. Headspace air from the centrifuges was drawn through the building's foul-air-collection system for use as combustion air in the incinerator.

A sample of the feed sludge was collected from a sampling valve just prior to the centrifuge. Because the sample contained the polymer at this point, collection of a representative sample was difficult due to rapid separation of the flocculated solids from the liquid. The sample of centrifuge cake was collected from a sampling door in the chute conducting the solids to the conveyor. Centrate was collected from a valve at the building's sampling sink.

A sample of the foul air from the centrifuge was collected in a stainless steel canister attached to a port in the exhaust air duct. Air flow through the duct was estimated using a hot wire anemometer inserted through the port to measure the air velocity. Readings were taken at several locations across the pipe diameter to obtain a representative flow. A second sampling round was repeated approximately 2 hours after the first set of samples. The solids and foul air temperatures were 24°C.

The solids mass balance was established for the process based on measured flow of centrifuge feed and measured mass of sludge cake, expressed as dry solids, leaving the centrifuge for the incinerator. In Table 11.8, which summarizes the flows and concentrations in solids around the centrifuge, the total solids concentration in the centrifuge feed was considered low at 12,230 mg/L, half of the value of approximately 25,000 mg/L anticipated by plant staff. The probable reason for a low measured concentration was that the flocculating solids from the sampling valve by the centrifuge, which included the polymer, tended to separate very quickly from the accompanying water.

TABLE 11.7
Distribution of Representative VOCS Exiting the Ingersoll Filter Press

Contaminant	% of Total Output			
	Filtrate	Wash water	Cake	Air
Dichloromethane	13.40	0.00	86.37	0.23
Toluene	4.11	1.43	94.34	0.11
m,p-Xylene	5.54	2.62	91.46	0.39
3-Ethyltoluene	2.61	1.36	95.95	0.08
1,3,5-Trimethylbenzene	2.61	1.47	95.81	0.11
1,2,4-Trimethylbenzene	2.89	1.58	95.41	0.11
1,4-Dichlorobenzene	3.54	1.59	94.78	0.09

Monteith, H.D. and Bell, J.P., Modeling of VOC emissions from biosolids dewatering processes, *Proc. WEFTEC '98, Vol. 6. Facility Operations I & II.* 71st Annual Conference and Exposition, Water Environment Federation, Orlando, FL, October 3–7, 157–168, 1998. With permission

The mass balance for solids around the centrifuge is provided by the expression shown in Equation 11.5:

$$Q_{si}X_{si} = Q_{fil}X_{fil} + Q_{cak}X_{cak} \tag{11.5}$$

with

$$Q_{fil} = Q_{si} - Q_{cak}$$

Using the measured solids concentrations, the total outputs of the solids represented 183% of the input mass, an indication that the measured feed solids concentration may well be low. For estimation of mass balances, the flows were estimated from the solids balance using a more historical concentration of 24.5 g/L in the feed.

Mean VOC concentrations in the process streams in and out of the centrifuge are provided in Table 11.9. Contaminant concentrations were generally lower in the centrate than in the feed sludge. Toluene was by far the most abundant contaminant in all the matrices investigated. Other VOCs found at elevated levels in the cake and exhaust air were 1,2,4-trimethylbenzene and 1,4-dichlorobenzene.

The mass balance of VOCs around the centrifuge can be written as shown in Equation 11.6:

$$Q_{si}C_{si} = Q_{fil}C_{fil} + Q_{cak}C_{cak} + Q_GC_G \tag{11.6}$$

with the parameters as previously defined.

The mass balance closures of the VOCs were greater than 100%, similar to the findings with the filter press study. The most probable cause of the elevated closures resulted from the solids balance (i.e., low feed solids concentration); however, other

TABLE 11.8
Flow and Suspended Solids Concentrations in Centrifuge Process Streams

Stream	Flow (L/h)	Solids Conc. (g/L)
Feed sludge	37,800	12.234
Centrate	3,530	0.253
Cake	34,270	237.50

TABLE 11.9
Mean Concentrations of Representative VOCs in Centrifuge Process Streams

	Mean Concentration			
Contaminant	Feed (μg/L)	Centrate (μg/L)	Cake (ng/g)	Air (ng/L)
Dichloromethane	1780	2985	179500	85430
Toluene	0	0.68	33	633
m,p-Xylene	1.07	1.22	94.80	41.4
3-Ethyltoluene	2.58	2.97	314.5	783.5
1,3,5-Trimethylbenzene	0	3.32	824	194.0
1,2,4-Trimethylbenzene	7.62	6.58	1207.5	253
1,4-Dichlorobenzene	7.99	8.58	1012.5	226.5

Monteith, H.D. and Bell, J.P., Modeling of VOC emissions from biosolids dewatering processes, *Proc. WEFTEC '98, Vol. 6. Facility Operations I & II.* 71st Annual Conference and Exposition, Water Environment Federation, Orlando, FL, October 3–7, 157–168, 1998. With permission

errors may have been introduced if nonrepresentative samples were collected, or due to potential errors in the gas flow measurement.

Mass fluxes of the VOCs in the centrifuge process streams are presented in Table 11.10. The mass of each VOC in the foul air stream drawn through the centrifuge was estimated using a flow rate of 10.6 m3/h (6.24 cfm) based on the hot wire anemometer readings. Toluene was clearly the predominant VOC in the process streams; total outputs of toluene were over two orders of magnitude higher than the next highest compounds, 1,2,4-trimethylbenzene and 1,4-dichlorobenzene. From Table 11.10, it is also clear that the total output mass of each VOC substantially exceeds the input mass. This was interpreted as further evidence that the feed samples were nonrepresentative and low in suspended solids, to which the VOCs are sorbed.

TABLE 11.10
Mass Balance of Representative VOCs around the Highland Creek Centrifuge

Contaminant	Centrifuge Mass Balance (g/h) Feed	Centrate	Cake	Air	Total Out
Dichloromethane	67.3	102.3	150.7	0.906	253.9
Toluene	0.0	0.018	0.021	0.0067	0.046
m,p-Xylene	0.040	0.042	0.080	0.0004	0.122
3-Ethyltoluene	0.098	0.102	0.264	0.0083	0.374
1,3,5-Trimethylbenzene	0.129	0.114	0.692	0.0021	0.808
1,2,4-Trimethylbenzene	0.288	0.225	1.014	0.0027	1.242
1,4-Dichlorobenzene	0.302	0.294	0.850	0.0024	1.146

Monteith, H.D. and Bell, J.P., Modeling of VOC emissions from biosolids dewatering processes, *Proc. WEFTEC '98, Vol. 6. Facility Operations I & II.* 71st Annual Conference and Exposition, Water Environment Federation, Orlando, FL, October 3–7, 157–168, 1998. With permission

TABLE 11.11
Distribution of Representative VOCs in the Highland Creek Centrifuge Outputs

Contaminant	% of Total Mass Outputs Centrate	Cake	Air
Dichloromethane	40.3	59.4	0.4
Toluene	38.8	46.5	14.7
m,p-Xylene	34.2	65.4	0.4
3-Ethyltoluene	27.2	70.6	2.2
1,3,5-Trimethylbenzene	14.1	85.7	0.3
1,2,4-Trimethylbenzene	18.2	81.6	0.2
1,4-Dichlorobenzene	25.6	74.2	0.2

Monteith, H.D. and Bell, J.P., Modeling of VOC emissions from biosolids dewatering processes, *Proc. WEFTEC '98, Vol. 6. Facility Operations I & II.* 71st Annual Conference and Exposition, Water Environment Federation, Orlando, FL, October 3–7, 157–168, 1998. With permission

The distribution of VOCs in the outputs from the centrifuge is summarized in Table 11.11. More than 2% of the total output mass of m,p-xylene was present in the exhaust air, ranging up to a maximum value of 14% for benzene. A greater proportion of individual VOCs was found in the gas phase from the centrifuge than was observed with the filter press. There are two potential explanations. First, the solids in the centrifuge are delivered to the revolving bowl through a pipe, creating a stream of sludge, which may also splash and shear at the bowl surface, tending to enhance mass transfer. With the filter press, the solids are deposited on the belts through a distribution header and then positioned on the belt by rows of spindles for even coverage of the belt. The surface area for mass transfer is much lower than that created by the nozzle in the centrifuge. A second explanation may be the foul air flow through the centrifuge, which may be sufficient to prevent saturation of the headspace air and contribute to improved mass transfer. In the study, only a low flow sweep air was applied to the belt filter press.

Based on the equipment dimensions and headspace within the two units, however, the turnover time of headspace volumes is believed to be less for the centrifuge than the filter press and its enclosure. In normal operation of the filter press at Ingersoll, the air movement around the unit due to the ceiling exhaust fan would probably tend to increase the overall mass emissions, but this could not be measured.

The mass of VOCs in the centrate returned to the plant is significant. The mass of VOCs in the centrate as a percentage of the total outputs ranged from 18% for 1,2,4-trimethylbenzene to 40% for toluene. The cake solids typically retained the majority of the VOC mass (47 to 86%), but not to the extent observed with the filter press cake (which was typically greater than 85% of total output).

Two approaches were taken by Monteith and Bell[5] in trying to relate emissions of VOCs from the belt press and centrifuge to specific VOC properties. In the first approach, the emission of a VOC was expressed as a function of Henry's law coefficient, according to the relationship shown in Equation 11.7:

$$EF = 1 - e^{-aH_c} \tag{11.7}$$

where

EF = fraction of contaminant mass in feed emitted from process
H_c = Henry's law coefficient, L_{liq}/L_{gas}
a = fitting parameter

The form of this relationship limits the fraction emitted to 100% as Henry's Law coefficient tends to infinity. The results of the modeling for the filter press and centrifuge, respectively, are provided in Figures 11.3 and 11.4. The fitted parameter "a" from this exercise for the processes is presented in Table 11.12. The values of "a" were very similar, at 0.00587 and 0.00560 for the belt press and centrifuge, respectively. The modeling indicated that, over the range of Henry's Law coefficients measured, the relationship was essentially linear for both dewatering processes. Based on this observation, a linear relationship was tested of the form shown in Equation 11.8:

$$E = mH_c \tag{11.8}$$

where

m = fitting parameter

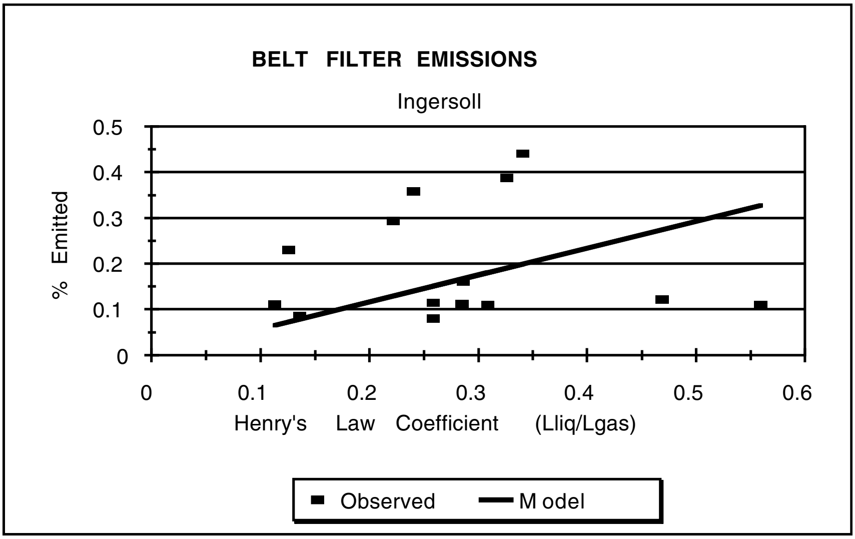


FIGURE 11.3 Observed and estimated emissions from Ingersoll filter press. Monteith, H.D. and Bell, J.P., Modeling of VOC emissions from biosolids dewatering processes, *Proc. WEFTEC '98, Vol. 6. Facility Operations I & II.* 71st Annual Conference and Exposition, Water Environment Federation, Orlando, FL, October 3–7, 157–168, 1998. With permission.

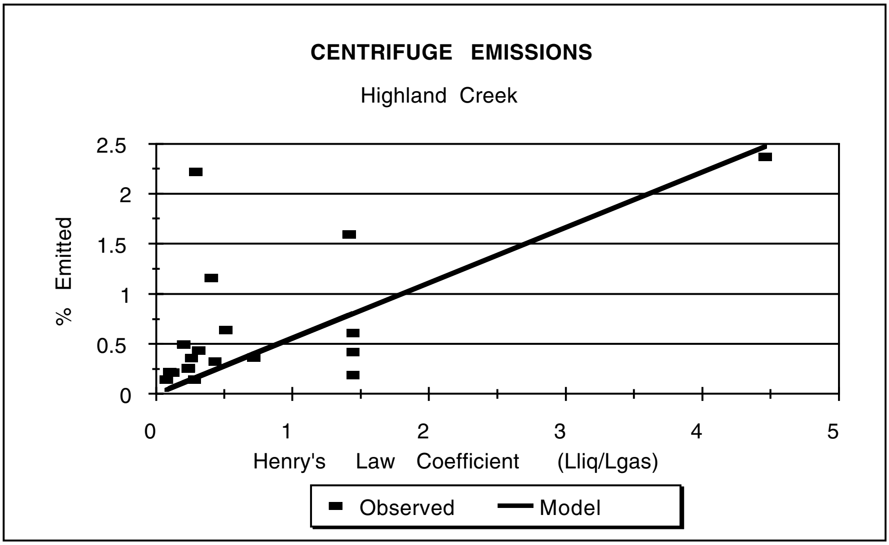


FIGURE 11.4 Observed and estimated emissions from Highland Creek centrifuge. Monteith, H.D. and Bell, J.P., Modeling of VOC emissions from biosolids dewatering processes, *Proc. WEFTEC '98, Vol. 6. Facility Operations I & II.* 71st Annual Conference and Exposition, Water Environment Federation, Orlando, FL, October 3–7, 157–168, 1998. With permission.

TABLE 11.12
Parameter Estimate for Fraction of VOC Emitted in Sludge Dewatering

Process	Fitting Parameter "a"
Belt press	0.00587
Centrifuge	0.00560

Monteith, H.D. and Bell, J.P., Modeling of VOC emissions from biosolids dewatering processes, *Proc. WEFTEC '98, Vol. 6. Facility Operations I & II.* 71st Annual Conference and Exposition, Water Environment Federation, Orlando, FL, October 3–7, 157–168, 1998. With permission

An inherent danger in this type of relationship is that the fraction emitted may not be limited to 1.0, especially for highly volatile compounds. The slope and r^2 values for the linear regression analysis for the filter press and centrifuge are presented in Table 11.13. The slope of regression lines for the two processes is very similar, an indication that emissions from the two processes have a similar dependence on Henry's Law coefficients. Neither the r^2 values nor the standard error of the zero intercept are consistent between the processes, however, with the filter press having a larger value of r^2, and a smaller value of the standard error of the intercept, than the centrifuge. This may be due to the smaller range of H values in the filter press data (i.e., 0.1 to 0.6 L_{liq}/L_{gas}) than in the centrifuge data and to the presence of one data point's deviating more widely than the others at a H_c value of 0.3 in the centrifuge data.

TABLE 11.13
Linear Regression Parameters for Emissions from Dewatering Processes

Process	Filter Press	Centrifuge
m, fitting parameter	0.586	0.570
Std error of m	0.129	0.113
r^2	0.403	0.190
Intercept	0	0
Std error of intercept	0.148	0.615

Monteith, H.D. and Bell, J.P., Modeling of VOC emissions from biosolids dewatering processes, *Proc. WEFTEC '98, Vol. 6. Facility Operations I & II.* 71st Annual Conference and Exposition, Water Environment Federation, Orlando, FL, October 3–7, 157–168, 1998. With permission

The fraction of total output in the gas phase was also plotted against the solid/liquid partition coefficient (K_p) to evaluate any potential effect of the sorption to solids on VOC emissions. One would expect an inverse relationship to exist, as emissions should be lower if the partition coefficient rises (i.e., more is associated with the solid phase). Over the range of K_p values detected in the process streams (0.1 to 3.6 L/g VSS), there was no apparent relationship between the fraction emitted and the K_p value.

A final attempt was made with the filter press data to derive a more mechanistic mass transfer model incorporating an overall mass transfer coefficient, K_L. However, upon a preliminary investigation of the data, there was no evidence that this approach would lead to any greater accuracy in predicted emissions than the models presented either as Equations 11.7 or 11.8.

Based on the form of the emission factor equations, the exponential model, as described in Equation 11.7, was selected as the preferred model because the factor could not rise above a value of 1.0.

Emissions from the dewatering units are a small component of the mass in the unit feed stream and thus would be a very small component of overall wastewater treatment facility emissions. The main concern with emissions from dewatering devices would relate to potential health concerns of operators working in proximity to the dewatering processes for extended periods.

11.5 SUMMARY

Only a few studies have investigated the emissions of VOCs from wastewater solids dewatering devices. No studies have been sufficiently rigorous to permit calculation of mass transfer parameters for the dewatering units. Empirical emission factors incorporating Henry's Law coefficient have been derived for belt filter presses and centrifuges. In general, most of the VOCs entering the dewatering unit in the feed solids remain with the cake solids, and emissions of VOCs from the dewatering processes are small, especially when compared with emissions from the other wastewater treatment processes.

REFERENCES

1. Parker, W.J., Thompson, D.J., Bell, J.P. and Melcer, H., Fate of volatile organic compounds in municipal activated sludge plants, *Water Environ. Res.*, 65(1), 58, 1993.
2. Parker, W.J., Monteith, H.D. and Melcer, H., VOCs in fixed film processes. II: model studies, *J. Environ. Eng., ASCE*, 122(7), 564, 1996.
3. Parker, W.J., Monteith, H.D. and Melcer, H., Preliminary assessment of the removal of volatile organic compounds in a biological selector process, *Water Environ. Res.*, 67(5), 798, 1995.
4. Parkin, G.F., Anaerobic biotransformation of chlorinated aliphatic hydrocarbons: Ugly duckling to beautiful swan? *Proc. WEFTEC '97, Volume 1, Part 1: Research.* Chicago, October 18–22, 1. Water Environment Federation, Alexandria, Virginia, 1997.

5. Monteith, H.D. and Bell, J.P., Modeling of VOC emissions from biosolids dewatering processes, *Proc. WEFTEC '98, Vol. 6. Facility Operations I & II.* 71st Annual Conference and Exposition, Water Environment Federation, Orlando, FL, October 3–7, 157–168, 1998.
6. Wilson, S.C., Burnett, V., Waterhouse, K.S. and Jones, K.C., Volatile organic compounds in digested United Kingdom sewage sludges, *Environ. Sci. Technol.*, 28(2), 259, 1994.
7. Webber, M.D., Rogers, H.R., Watts, C.D. Boxall, A.B.A., Davis, R.D. and Scoffin, R., Monitoring and prioritization of organic contaminants in sewage sludges using specific chemical analyses and predictive non-analytical methods, *Sci. Total Environ.*, 185, 27, 1996.
8. Montgomery, J. M., PEEP Final Report for Publicly Owned Treatment Works. Submitted to Joint Powers Agencies, by James M. Montgomery Consulting Engineers, Pasadena, California, 1990.
9. API, *Evaluation of the Technology Alternatives for Controlling Fugitive Emissions from Sludge Dewatering Operations,* API Publication No. 4566, Health and Environmental Sciences Dept., American Petroleum Institute, Washington, D.C., 1992.
10. Ponder, T.C., Jr. and Bishop, C.J., Field assessment of air emissions from hazardous waste dewatering operations, *Proc. Sixteenth Annual Hazardous Waste Research Symposium, Cincinnati, OH. EPA Report No. EPA/600/9-90/037.* Risk Reduction Engineering Laboratory, Cincinnati, OH, 87–96, 1990.
11. Caballero, R.C. and Griffith, P., VOC emissions from POTWs. Paper presented at WPCF/EPA Workshop on Air Toxics Emissions and POTWs, Alexandria, Virginia, 1989.
12. Lauria, J. et al. An integrated approach to air toxics emissions control at a large publicly owned treatment works. Paper presented at WPCF/EPA Workshop on Air Toxics Emissions and POTWs. Alexandria, Virginia, 1989.

12 Sampling and Analytical Methods for Hazardous Air Pollutants

Farhana Mohamed, Prakasam Tata and Ing-Yih Cheng

CONTENTS

12.1 Introduction 191
12.2 Sampling Methodology 191
  12.2.1 Liquid Sampling 192
  12.2.2 Solids Sampling 192
  12.2.3 Sampling for Ambient Air and Non-Combustion Point Sources 192
    12.2.3.1 Canisters 194
      12.2.3.1.1 Canister Sampling at Subatmospheric Pressure 194
      12.2.3.1.2 Canister Sampling at Atmospheric Pressure1 195
    12.2.3.2 Tedlar® Bags 196
    12.2.3.3 U.S. EPA Surface Emission Isolation Flux Chamber 197
    12.2.3.4 Wind Tunnel 198
    12.2.3.5 Sorbent Tubes 200
  12.2.4 Sampling of Combustion Sources 200
  12.2.5 Compositing Methodology for Liquid VOC Samples 202
  12.2.6 Compositing of Air Samples 204
12.3 Analytical Methodology 205
  12.3.1 U.S. EPA Method TO-14 206
    12.3.1.1 Scope and Application 206
    12.3.1.2 Method Summary 206
    12.3.1.3 Interferences and Their Control 206
  12.3.2 U.S. EPA Method 18 208
    12.3.2.1 Scope and Application 208

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

- 12.3.2.2 Method Summary 208
- 12.3.2.3 Interferences and Their Control 208
- 12.3.3 SW 846 Method 8260 B 208
  - 12.3.3.1 Scope and Application Method 208
  - 12.3.3.2 Method Summary 208
  - 12.3.3.3 Interferences and Their Control 209
- 12.3.4 U.S. EPA Method 25 C 209
  - 12.3.4.1 Scope and Application 209
  - 12.3.4.2 Method Summary 210
  - 12.3.4.3 Interferences 210
- 12.3.5 SW-846 Method 8270 C 210
  - 12.3.5.1 Scope and Application 210
  - 12.3.5.2 Method Summary 210
  - 12.3.5.3 Interferences and Their Control 210
- 12.3.6 SW-846 Method 8280 A 211
  - 12.3.6.1 Scope and Application 211
  - 12.3.6.2 Method Summary 211
  - 12.3.6.3 Interferences and Their Control 211
- 12.3.7 CARB Method 429 212
  - 12.3.7.1 Scope and Application 212
  - 12.3.7.2 Method Summary 212
  - 12.3.7.3 Interferences and Their Control 212
- 12.3.8 CARB Method 430 214
  - 12.3.8.1 Scope and Application 214
  - 12.3.8.2 Method Summary 214
  - 12.3.8.3 Interferences and Their Control 214
  - 12.3.8.4 Method CARB 430 vs. FTIR Method 214
- 12.4 Quality Assurance 216
  - 12.4.1 Representativeness 216
  - 12.4.2 Sample Integrity 216
  - 12.4.3 Sample Chain-of-Custody 216
  - 12.4.4 Field Blanks and Duplicates 217
  - 12.4.5 Sample Transport 217
- 12.5 Analytical Procedures and Calibration Frequencies 217
  - 12.5.1 Analytical Procedures 217
  - 12.5.2 Laboratory Standards, Specialty Gases and Reagents 217
  - 12.5.3 Calibration Procedure and Frequency 217
  - 12.5.4 Analytical Quality Control Samples 218
- 12.6 Method Detection Limits and Reporting Levels 218
  - 12.6.1 Achieving lower MDLs in Various Matrices 218
  - 12.6.2 Guidelines for Reporting Data Below Detection Levels for Risk Management and Potential Health Risk Assessments (HRAs) 219
- 12.7 Perspective and Connectivity 221
  - 12.7.1 Use of Direct Assessment Techniques for Risk Assessment 221

12.7.2 Traditional and Performance-Based Regulatory Compliance Monitoring....222
12.8 Summary....223
References....223

12.1 INTRODUCTION

During the establishment of MACT standards for POTWs under Title III of the CAAA, controlling the emissions of HAPs has been a regulatory priority. For instance, several state and air district regulations such as the California's Air Toxics "Hot Spots" Information and Assessment Act of 1987[1] and South Coast Air Quality Management District (SCAQMD) Rules 1179,[2] 1401[3] and 1402[4] require accurate emission inventory and quantification of air toxics emissions from POTWs to determine their impact on human health. In some cases, direct test data from liquid samples were used to develop emission factors for estimating the emissions from POTWs. In such instances, the importance of sampling and analytical methods cannot be overemphasized. In addition, direct air emission data are needed for permit compliance monitoring, calculating the mass emission rates and evaluating the efficiency of wastewater treatment processes, scrubbers and combustion sources such as boilers, flares, gas turbines, internal combustion engines and sewage sludge incinerators.

In the modern-day POTWs, samples from different matrices such as liquid, solid and air are collected and analyzed for the control of treatment processes and for regulatory compliance. While most treatment plants depend on the operation personnel for collection of samples, few plants have properly trained staff to collect air samples for analysis of HAPs. Despite the time-tested fact that an environmental sample analysis is as good as the sampling, municipal agencies have rarely trained engineering or laboratory personnel who are well versed in the significance of representative sample collection for HAPs and selection of proper analytical methods and quality assurance protocol.

This chapter provides a summary and references to appropriate analytical methodology for the quantitation of HAPs supplemented by actual POTW sampling projects, and focuses on the pitfalls to avoid and important precautions to take to get meaningful analytical results. The guidelines presented in this chapter are recommended for collecting and analyzing liquid, solid and gaseous samples for analysis of volatile and semivolatile HAPs.

12.2 SAMPLING METHODOLOGY

Prior to sampling, it is important to set up a matrix-specific sampling plan. The purpose is to collect representative environmental samples (e.g., influent, effluent, sludge, headspace air, other gaseous samples, etc.) to ensure integrity and completeness of analytical results. Frequency of sampling, with special consideration to temporal and diurnal effects, use of approved and validated sampling and preservation techniques, and analytical methods are important for maintaining sample representativeness and integrity. Plans for collecting wastewater, hazardous- and solid waste and air samples can be obtained from several standard texts.[5,6] Typical sampling procedures are listed in Table 12.1.

12.2.1 LIQUID SAMPLING

Wastewater systems vary in composition at different time intervals, necessitating sample collection at a representative point, and are "time composited" by collecting grab samples at well-spaced intervals for truly representative samples. Plant personnel need to be in contact with each other to get information on process flow data and any plant upsets that might compromise representative sampling. Wastewater or liquid samples should be collected over a period of time, which takes into account retention time for different processes. In some cases, representative samples are collected in different seasons to account for any seasonal variation. Liquid samples for VOC analysis are collected as grab samples with a bucket or dipper bowl at specific time intervals in glass vials (50 mL or less) with no headspace or air bubbles.[5] For samples containing very low VOC concentrations, extra precautions are needed to maintain sample integrity. Grab samples are then carefully composited proportional to the flow rate at the sampling point. Instead of grab samples, a continuous zero head sampler has been used by certain laboratories. A 5-L Tedlar® bag in an ice cooler is used to collect a liquid sample at sampling rate of 2 mL/min.[1] The samples are collected through a continuous sampler using a peristaltic pump. Samples are then carefully transferred into vials for analysis. Wastewater treatment samples for organic analysis need to be properly preserved (pH < 2, storage at 4°C) prior to analyses. All samples should be analyzed within 14 and 7 days for volatile and semivolatile organic compounds, respectively, after sample collection.

12.2.2 SOLIDS SAMPLING

Most POTWs dewater digested sludge (4 to 5% solids) through mechanical means (e.g., centrifugation, belt processes, etc.) and beneficially use the product (biosolids, > 20% solids). Sewage sludge, biosolids and other related sludge products are analyzed for metals, VOCs and other organic constituents for compliance with several federal and state regulations. Solid or semisolid samples from sludge treatment processes such as lagoons, ponds, tanks, centrifuges and air-drying beds are collected at various solids-handling facilities or as grab samples either in 40-mL glass vials or in 0.5-L glass bottle and preserved at 4°C prior to analyses. The sample collection and preservation procedure is similar to that used for collecting liquid samples described above.

12.2.3 SAMPLING FOR AMBIENT AIR AND NON-COMBUSTION POINT SOURCES

In this section, direct and indirect emission sampling and analytical methodologies are addressed. Most often, except for the flux chamber, all other devices are used interchangeably for non-combustion point and nonpoint sources. Compared with the

TABLE 12.1
Sampling Procedures for HAPs

Matrix	POTW Source	Compounds	Sample Collection Method	Preservation/ Holding Time
Liquids	Wastewater processes (influent/effluent)	VOCs/organics	Amber glass vial or bottle, pH <2	4°C, 7–14 days
Solids	Sludge processes/biosolids/ grit	VOCs/organics	Amber glass bottle	4°C, 7–14 days
Ambient/near ambient gaseous samples	Open/enclosed surfaces, scrubber ducts	VOCs/organics	Summa canister	14 days, cool storage, avoid sunlight
	Open liquid and solid surface emissions	VOCs	Flux Chamber	
		VOCs	Tedlar® bag-iron lung/CARB 422	72 h
Point source/ Combustion sources	Boilers, internal combustion engines, flares, gas turbines, furnaces, incinerators	Principal organic hazardous constituents (POHC)	SW-846 M0040	
		VOCs	VOST/SW-846 M0030/EPA Method 18/ CARB 422	7–14 days (preserved samples)
		VOCs, not applicable to polar or reactive VOCs	SMVOST/SW 846 M0031	7 days (preserved samples)
		Aldehydes	DNPH cartridge/ SW-846/ CARB 430	4°C, extraction in 7 days, analysis 30 days
		Polynuclear aromatic hydrocarbons (PAH), phenol	Sampling train/CARB 429	4°C, extraction in 14 days
	Stacks	Modified Method 5 sampling train for particulate emissions	SW-846 M0010	NOx can interfere with some organics in presence of moisture
		Dioxins	SW-846 M0023A	4°C, extraction in 14 days

sampling and analysis of liquid and solid samples at POTWs, sampling and testing methodologies for point sources and ambient (whole) air are relatively unestablished. Very limited data are available from direct measurements of air emissions at the POTWs. During the development of MACT standards for POTWs, U.S. EPA solicited direct source test data from wastewater collection and treatment systems.[7]

For representation, the air samples are usually collected over a longer period of time to account for overriding spikes and unusual events. Selecting a site for ambient air sampling, meteorological data, terrain and distance from source for impact of emissions is of utmost importance. For sample collection at stationary point sources, sample location and velocity traverse points are determined according to U.S. EPA Method 1 (Detection of sample port locations and velocity traverse points for stationary sources). For gas velocity and flow rate, U.S. EPA Method 2 (Detection of stack gas velocity and volumetric flow rate (S-type Pitot tube) for stationary sources) is used. The near ambient samples for non-combustion sources at POTWs do not usually require U.S. EPA Method 3 (Gas analysis for dry molecular weight) and U.S. EPA Method 4 (Detection of moisture content in stack gas) determinations. For ambient and head-space air samples from wastewater treatment plants and other non-combustion sources, the following devices are generally used.

12.2.3.1 Canisters

Air samples are collected in specially treated Summa passivated canisters. Canister sampling, while recommended for ambient sampling, has also been used for non-combustion, near-ambient air point sources where there is less likelihood of condensation. In POTWs, it can be used at all open surfaces, tanks and headwork ducts and flux chamber offgas samples. However, U.S. EPA Method 18 does not allow the use of canisters when sampling for combustion or non-combustion point sources.[8] Only Tedlar bags or adsorbent tubes are allowed in Method 18 due to moisture condensation problems in the canisters. Due to problems associated with condensation of moisture, canister sampling should not be used for combustion sources or where the exhaust gas moisture levels are not at par with the ambient levels. In some instances, when sampling from ducts, a moisture knockout impinger is used before the canister for avoiding transfer of moisture into the canister. When in doubt, it is important to confirm with the U.S. EPA or local regulators for appropriateness of using canister sampling.[9] The samples are analyzed for VOCs by passing them through a dryer to a cryogenic trap followed by thermal desorption onto a fused-silica capillary gas chromatography (GC) column. Typical method detection limits (MDLs) by canister method for volatile organic HAPs (VOHAPs) range from <5 ppbv to 0.005 ppbv using a GC/flame ionization detector (FID)-photoionization detector (PID)-electrolytic capture detector (ELCD). The GC/mass spectrometer (MS) method such as TO-14 can also be used but MDLs are somewhat higher. (See Method TO-14 in Section B.1, Analytical Methodology.) Canister samples should be analyzed within 14 days.

12.2.3.1.1 Canister Sampling at Subatmospheric Pressure

Canister sampling is done under vacuum (subatmospheric pressure, 0.05 mmHg) when samples are grab- or time-integrated for not more than 24 h. In the latter case, samples are collected through mass flow controllers or some other flow controller device. Due to the differential pressure, the air sample flows into the canister under positive pressure and a sampling pump is not necessary. The flow controllers used with the evacuated canisters need to be calibrated prior to each sampling event with a gas flow calibrator. This calibration is required under Method TO-14 (see Method TO-14 in Section 12.3.1, Analytical Methodology) to assure constant flow in the evacuated canister during ambient air sampling. Calibration is done with ultra-pure air. In-field calibration is also required before the sampling and every 2 to 3 h thereafter to ensure constant flow in the canister. For analysis, canister samples under subatmospheric pressure need to be pressurized between 15 to 30 psi. The dilution effect is corrected by measuring the gas pressure before and after pressurization (Figure 12.1). The pressurization is done by using ultra-high-purity nitrogen to minimize matrix reaction effects and to dilute oxygen and moisture contained in the sample.

12.2.3.1.2 Canister Sampling at Atmospheric Pressure

Pressurized canister sampling is used when long-term integrated samples or high-volume samples are needed. The sample is collected in a canister using a pump and flow control arrangement. The pressure is usually below 30 psi. By adjusting the flow rate, air samples can be collected for 24 h or beyond.

The canisters are useful for collection of samples containing highly VOCs over a period of 8 to 24 h. If a membrane dryer is being used for moisture collection, interferences may occur during analysis. To avoid sample contamination, it is necessary to clean canisters prior to use — preferably by employing a commercial canister cleaning system with a vacuum of <0.05 mm Hg to <0.1 mmHg such as the cleaning system by Entech Instruments.[10] Such cleaning systems are capable of cleaning multiple canisters.

12.2.3.2 Tedlar® Bags

Air sample bags made from Tedlar® polymer and fitted with Teflon valves are a popular and convenient device for HAPs sampling for stationary and fugitive point sampling (e.g., sampling ports at various treatment processes and scrubber outlets) at wastewater treatment plants. U.S. EPA and California Air Resources Board (CARB) have validated Tedlar® bags for sampling of VOCs.[11] In a typical case, the plant offgas samples are collected in accordance with the CARB Method 422, using an iron lung (IL), which consists of a pressure gauge, vacuum pump, flow meter, needle valve and Swagelock high-pressure fittings. All sample lines are 1/4-in-diameter Teflon tubing. Using the pump, the sample line is purged with the process offgas. The vacuum line is connected to the IL and the sample line is connected to a Tedlar® bag positioned inside. Once the IL is evacuated, offgas flows into the Tedlar® bag under positive pressure. At the end of the sampling period, the sample and vacuum lines are disconnected from the bag and IL (Figure 12.2). Most of the

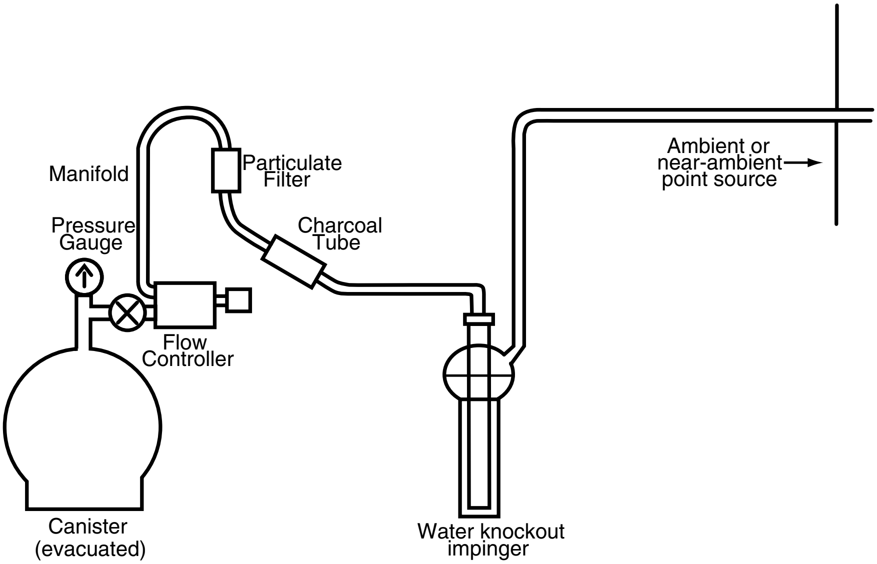


FIGURE 12.1 Summa canister sampling system schematic. (Modified from U.S. EPA, Compendium of Methods for Determination of Toxic Compounds in Ambient Air (EPA-600/4-89-017 and Supplements: 600/4-87-006, 600/4-87-013), Research Triangle Park, North Carolina, 1989.)

samples are collected over a period of 2 to 4 h for units such as a scrubber. Inlet and outlet air samples are collected at the same time. The sample holding time in Tedlar® bag is 72 h. This method is suitable for determining VOCs in 1 ppb to 200 ppm range and is not recommended for compounds with a high molecular weight or very low vapor pressure. For sampling combustion sources using Tedlar® bags, it is necessary to find out stack temperature for the selection of the proper probe and to calculate the moisture content.

12.2.3.3 U.S. EPA Surface Emission Isolation Flux Chamber

The theory behind the flux chamber emission measurement device is to allow for the direct measurement of gaseous emissions from open surfaces such as spills, open liquid and solid surfaces, landfills, aeration tanks, grit chambers, sludge drying beds and lagoons.

The flux chamber method involves direct measurement of emissions in an enclosed space. It is most effective for measurement of volatile organic and sulfur-containing compounds. This is done by measuring surface area, flow rate and effluent concentration.[1,12] This device has been successfully used to measure emission rates from all open liquid and solid surfaces such as headworks, channels and primary, secondary and tertiary treatment processes at POTWs (Figure 12.3).

The operation of a flux chamber involves:

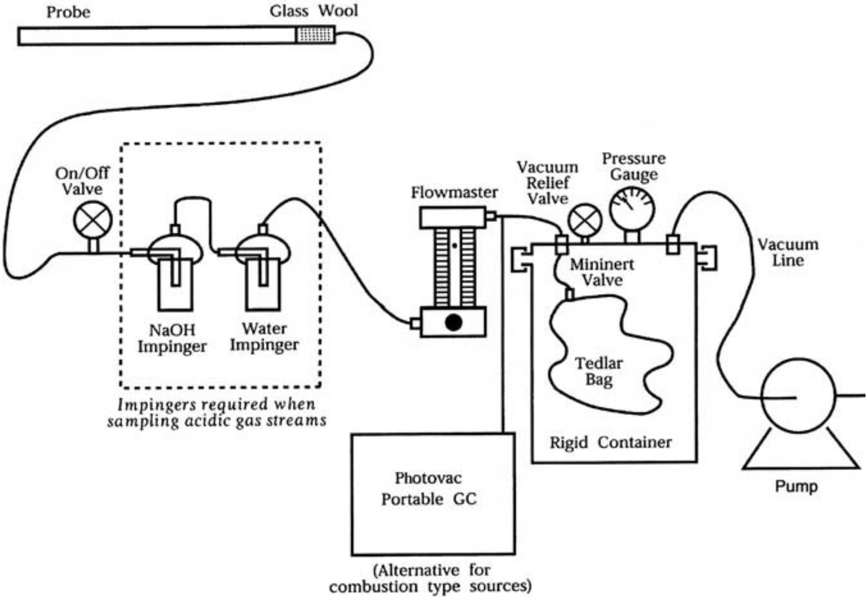


FIGURE 12.2 CARB Method 422 sampling train. (California Environmental Protection Agency, State of California Air Resources Board, CARB Method 422, Stationary Source Test Methods, Determination of VOCs in Emissions from Stationary Sources, Monitoring and Laboratory Division, Sacramento, California, Amended Dec. 1991.)

- Identifying the test area
- Ensuring that the stainless steel or plexiglass chamber rests or floats on the surface
- Initiating sweep gas flow rate to the flux chamber
- Collecting exhaust gas for analysis
- Decontaminating the chamber
- Relocating the measurement equipment to the next test area

It is important to have enough sampling locations to allow the total emissions from the emitting surface area to be calculated.

Flux chamber technology is best applicable to sludge lagoons, grit chambers and any other open land surface at a POTW. One of the precautions for using flux chambers is to avoid any surface disturbance during the placement of the chamber for representative emissions. For ponds, lagoons and final clarifiers, the chamber should be carefully suspended on the liquid surface to avoid negative bias in the data by liquid entrapment. For aeration tanks and other mixed liquid surfaces, emission rates from different zones need to be calculated. For sampling open wastewater treatment tanks, depth and potential loss of VOCs due to turbulence must be considered. Fugitive emissions from valves and ports of various emission devices such as tanks and emission control devices can also be assessed from flux chambers.

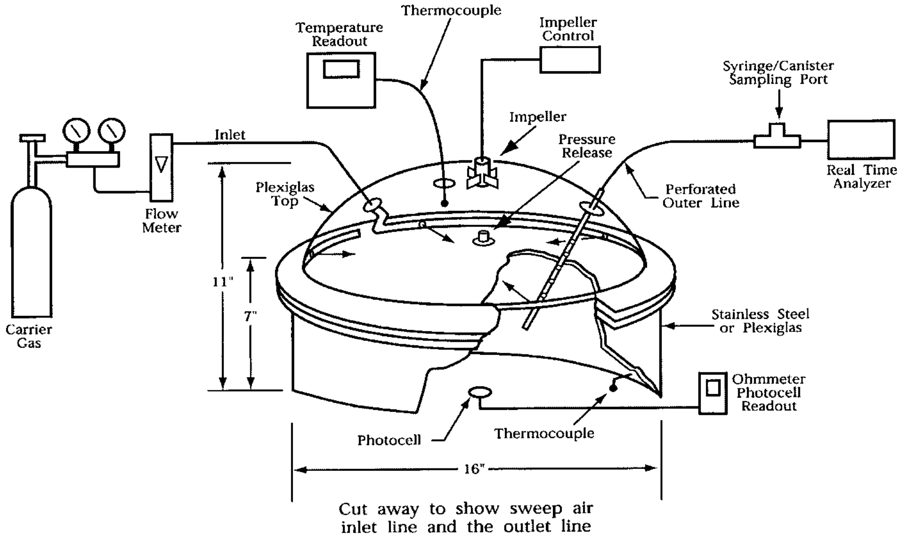


FIGURE 12.3 Diagram of USEPA surface emission isolation flux chamber at POTWs. (Schmidt, C.E., Theory and operation of the U.S. EPA Surface Emission Isolation Flux Chamber at POTWs. Training Course for Bureau of Sanitation, City of Los Angeles, July, 1994.)

However, it is critical to identify zones of similar emission potential to quantify gaseous leaks.[13]

12.2.3.4 Wind Tunnel

In recent years, a portable wind tunnel has been developed for measuring odor emission rates and collecting gaseous samples from area sources such as sludge lagoons, compost facilities, agricultural farms, spill sites and landfills.[14] The system typically includes an external fan, an activated carbon filter and a stainless steel wind tunnel enclosure. The enclosure consists of a main section, an extension inlet duct, an expansion section, a contraction section, a mixing chamber and a couple of hollow tubes to enable the floating of the wind tunnel in a lagoon or an aeration tank (Figure 12.4).

The sampling hood of the wind tunnel covers a known surface area of the unit process from which the emission rate of volatile compounds needs to be measured. As measurements in the wind tunnel are based on boundary layer theory, it is very important to ensure that the aerodynamic performance in the main section is stable and that internal airflows are parallel. The extension inlet duct and expansion section are designed to improve aerodynamics in the main section. Vertical flat vanes are placed inside the expansion section to further improve the internal airflow. A perforated baffle is placed between the expansion section and the main section to prevent potential rotation of flows. The contraction section provides an opportunity for the mixing of odorous gases or VOCs and clean air. The mixing chamber, with a smaller cross-sectional area and a higher air velocity, further enhances the mixing. Part of

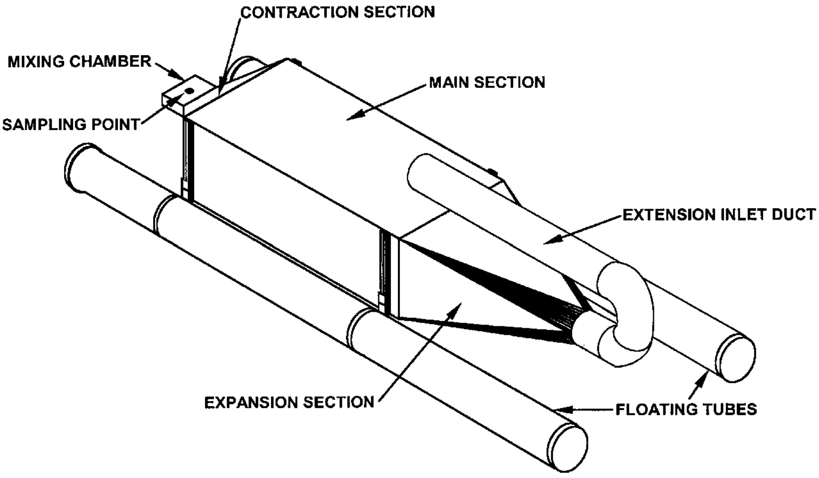


FIGURE 12.4 Portable Wind Tunnel.

the air mixture is taken from the mixing chamber via a sampling point. The hollow tubes allow the wind tunnel to float on liquid surfaces. When emissions are to be measured from solid surfaces, the hollow tubes are removed and the wind tunnel is directly placed on a flat area.

To determine an odor or VOC emission rate from an area source, a wind tunnel is placed on the surface of the source. A stream of activated carbon-filtered air or nitrogen gas is supplied into the wind tunnel to simulate parallel winds blowing on the main section or sampling hood. The sweep air velocity through the wind tunnel ranges from 0.2 to 0.65 m/s, with the optimum velocity of 0.3 m/s.[15] When the air stream flows across the odor- or VOC-emitting surface, convective mass transfer takes place above the surface. The emissions from the surface are carried by the air stream out of the sampling hood into the contraction section, where the odor- and VOC-free air is mixed with the gaseous emissions from the liquid or solid surface. The mixture of gases passes through the mixing chamber, where a portion of the mixture is withdrawn into a Tedlar® bag via teflon tubing. Volumetric flow rate of the sweep air through the wind tunnel is recorded and odor or VOC concentration in the collected emissions is measured using appropriate analytical techniques. For odor and VOC emission rate determinations, respectively, an olfactometer and GC/MS are used. The emission rates can then be calculated as shown in Equation 12.1.

$$\text{Emission rate} = \text{Odor or VOC concentration} \times \text{sweep air flow rate/} \\ \text{Exposed area of wind tunnel sampling hood} \qquad (12.1)$$

where exposed area is a product of the width and length of the wind tunnel sampling hood.

A recent study compared the features and performance of the flux chamber and wind tunnel for measuring emission rates from liquid and solid surfaces.[16] In this study, it was reported that the flux chamber is the only device accepted by the U.S. EPA for sampling emissions of direct measurements. Emission measurements may be overestimated by wind tunnels if adjustments of flow rate of headspace air and pressure are not properly made. Although wind tunnels are used in Australia and New Zealand for measurement of odor emissions, they are not widely used elsewhere for the determination of either odor- or VOC-emission rates.

12.2.3.5 Sorbent Tubes

Sorbent tubes or cartridges are also a convenient way to sample HAPs from ambient air and point sources for their detection at low detection levels. Various organic polymer adsorbents such as Tenax and XAD-2 resin or charcoal are used for sampling general-purpose organics.

An ambient air sample is drawn using a pump and then passed through an appropriate sorbent cartridge. The collected sample is later subjected to solvent extraction, or preferably thermally desorbed to recover VOHAPs of interest, which are then detected by GC/MS. While sorbent tubes offer a convenient method for sampling general-purpose organics, their retention in the polymer tubes may depend on the breakthrough volume and a possible chemical reaction with the sorbent. These problems can be mostly resolved by limiting the volume of the air drawn through the cartridge based on the compound with the smallest breakthrough volume. Suitable selection of a trap material such as 2,4-dinitrophenylhydrazine (2,4-DNPH) coated cartridges for aldehydes and ketones and XAD-8 resin for polar organics is important to avoid reaction of the trap material with the gas-phase organics.[16] The amount of sample collection in a sorbent trap is limited by the breakthrough of VOCs in a sorbent trap. The VOCs from a whole air sample can also be collected in a cryogenic sorbent trap, which not only concentrates the VOC samples at low levels but also results in reduced contamination with good recovery.[19]

For stationary sources, sorbent tubes such as 2,4-DNPH-coated cartridges are used for sampling aldehydes and ketones in CARB Method 430 and EPA SW 846 Method 0011 (Figure 12.5).[6,19] A Fourier transition infrared spectrophotometer (FTIR) method has been validated for combustion sources in accordance with the U.S. EPA Method 301 for formaldehyde, acetaldehyde, acrolein, CO, NO_x and CO_2.[20]

12.2.4 SAMPLING OF COMBUSTION SOURCES

At POTWs, various combustion devices such as gas turbines, boilers, internal combustion engines, flares and sewage sludge incinerators are tested regularly for process control and regulatory purposes. Combustion sources require more elaborate sampling than noncombustion sources. For calculation of mass emission rates, U.S. EPA Methods 1 to 4 are used for the determination of sample port locations and velocity traverse points, gas velocity and flow rate, stack gas velocity and volumetric flow rate (S-type pitot tube), dry molecular weight and moisture content for stack gases. Isokinetic sampling and particulate filter are used for detecting particulate matter from stack emissions. The target constituents are particulate matter, heavy metals and some organic compounds, such as formaldehyde, dioxin and furan, that are the by-products of com-

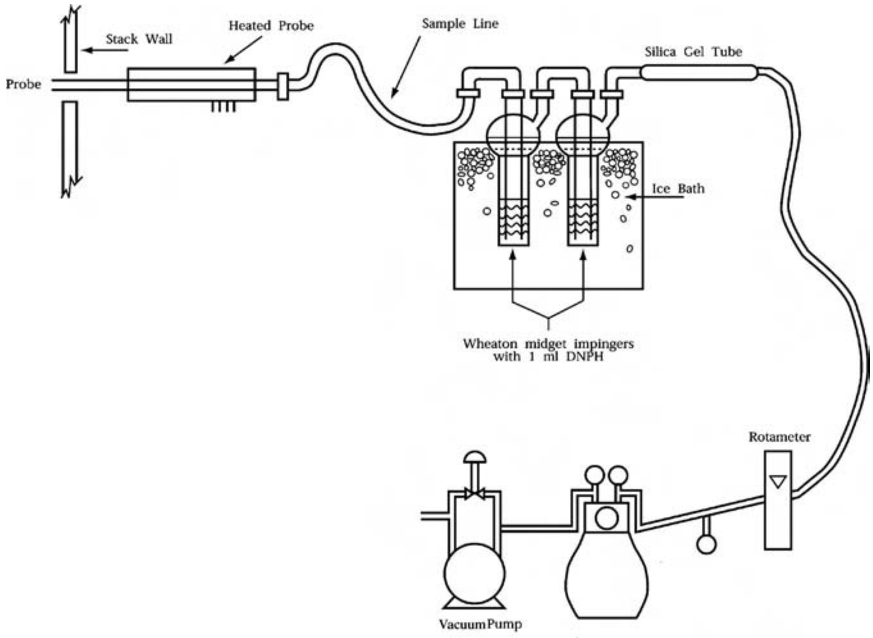


FIGURE 12.5 Schematic diagram of CARB 430 sampling system. (State of California Air Resources Board, CARB Method 430: Stationary Source Test Methods, Volume III, Methods of Determining Toxic Air Contaminants from Stationary Sources, Monitoring and Laboratory Division, Sacramento, California, September 1989.)

bustion. Some of these U.S. EPA Methods, such as Method 5, were modified by SCAQMD and usually involve more elaborate analysis and sampling. A nonisokinetic sampling train without particulate filters is used where little or no particulate matter is present in the exhaust gas and the emissions, such as VOCs, are in gas phase.

In addition, impingers and coated adsorbent tubes or cartridges are used for source sampling of ducts and stacks. For example, U.S. EPA Method 5 uses impingers for collection of filterable and condensable samples collected at combustion sources. For sampling using this method, a heated particulate filter and impingers (usually up to 4) are used. For the Modified Method 5 (SW-846 Method 0010), an XAD-2 sorbent resin bed is added for collection of these organics (Figure 12.6). Impingers are also used for capturing reactive organic compounds such as for volatile organic sampling train (VOST, SW-846 Method 0030), semivolatile organic sampling train (SMVOST, SW846 Method 0031) and selected aldehyde and ketone emissions (CARB Method 430 and SW-846 Method 0011) (Figure 12.7). Impingers may contain caustic, acid or reagents for collecting acidic, basic or organic oxidizing agents. Tedlar® bags are also used in the U.S. EPA SW-846 Method 0040 to collect principal organic hazardous constituents from combustion sources.

The VOST and SMVOST are used for collecting gaseous samples from stacks, internal combustion engines and gas turbine outlets. Usually, two sets of Tenax or other sorbent resin and charcoal traps are used (for general organic adsorption and

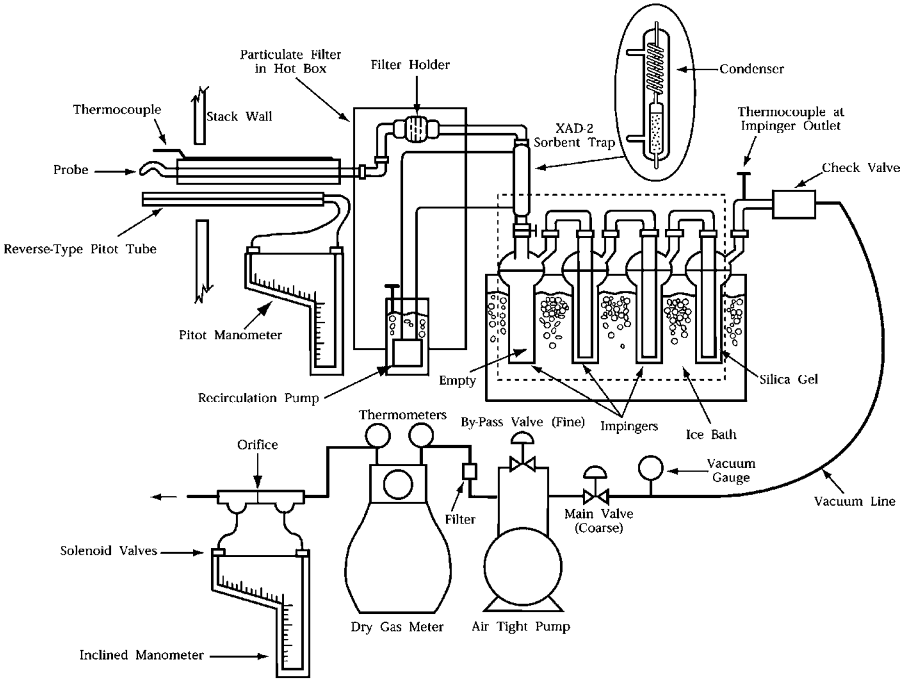


FIGURE 12.6 SW-846 Method 0010 Modified Method 5 sampling train. (U.S. EPA, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, 3rd ed., Publication No. SW-846, Office of Solid Waste & Emergency Response, Washington D.C., 1996.)

to avoid compound breakthrough). The Tenax trap is usually followed by a condensate trap to knock out moisture. The second sorbent device may follow a charcoal trap for absorbing organics in a VOST followed by a silica gel trap to absorb moisture. The SMVOST usually has a charcoal trap, condenser, two Tenax traps, a condensate trap followed by Anasorb and silica gel traps. Usually, traps are changed every 20 min during a 2-h sampling period.

12.2.5 COMPOSITING METHODOLOGY FOR LIQUID VOC SAMPLES

Information on the techniques for compositing grab samples of wastewater, sludge and air is relatively sparse. There are also no U.S. EPA approved methods. However, the EBMUD devised a method based on a simple concept. The method of sampling liquids based on this concept is approved by the U.S. EPA for volatile organic analysis (VOA) and is used in the autosamplers made by instrument companies such as Tekmar, Inc. This approach was taken in a recently completed study to determine VOC emission from all of the 14 wastewater treatment plants operated by New York City. In this study, the efficacy of the compositing techniques and the stability of the VOCs in the composited samples over a period of time were also determined. The study concluded that no statistically significant difference exists between the arithmetically derived average of the VOC concentrations of the individual grab samples and the VOC

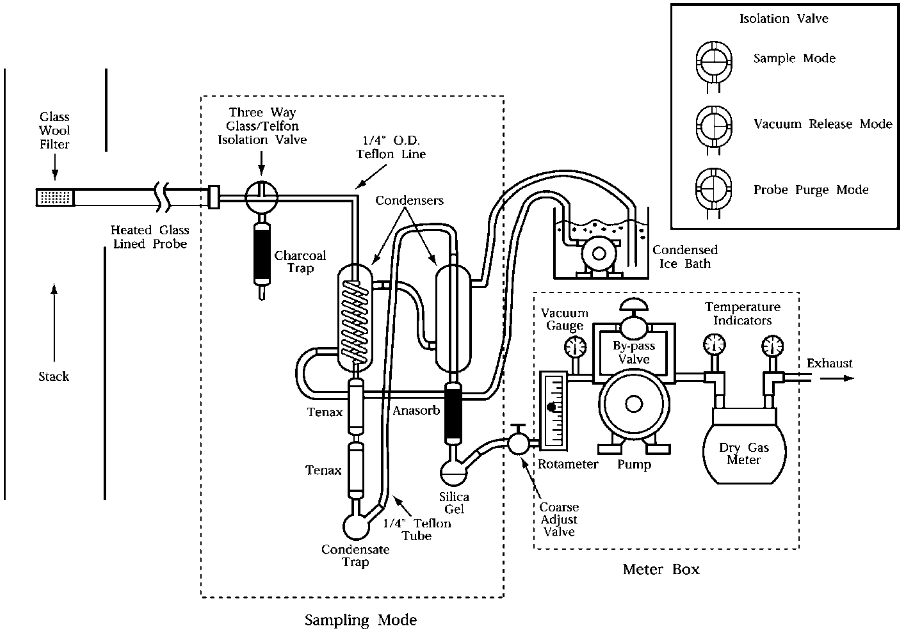


FIGURE 12.7 Schematic of sampling method for volatile organic compounds train. (U.S. EPA, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, 3rd ed., Publication No. SW-846, Office of Solid Waste & Emergency Response, Washington D.C., 1996.)

concentrations in the composites made from the grab samples.[20] This study also concluded that the VOC concentrations in the composited samples remained stable over a 4-week period.

The apparatus used for compositing the grab liquid samples collected in 40-mL VOA bottles in the above reported study is shown in Figure 12.8 and Figure 12.9. The compositing method consists of the following steps:

1. Invert the VOA bottles several times to ensure complete mixing before taking an aliquot from them for composting with other aliquots taken from other VOA vials.
2. Attach a 60-mL syringe to a three-way valve, close the valve and keep the syringe as the transfer syringe, into which aliquots taken from VOA bottles containing other grab samples will be transferred for compositing.
3. Equip the 60-mL syringe with a 10 cm needle, insert it into the top of the VOA bottle and open the valve to ensure the transfer of the wastewater from the VOA bottles containing the grab samples.
4. Insert a 30-mL syringe containing helium and equipped with a 1 cm needle into the VOA bottle as shown in Figure 12.8
5. Force exactly 5 mL of helium into the contents of the VOA bottle by pressing the plunger of the syringe, which will force 5 mL of the wastewater to enter into the transfer syringe.

6. Repeat this process with other VOA bottles after discarding the 1 cm needle from the 30-mL syringe each time after an aliquot is transferred into the transfer syringe.
7. When compositing of the various aliquots is completed, close the inlet valve of the 60-mL transfer syringe. The composite syringe is then placed in a chest containing ice packs and transported to the analytical lab. Instead of supplying the gas with a syringe as shown in Figure 12.8, it can be supplied to a valve and needle directly from a 10 psig helium gas source to displace the liquid from a sampling vial as shown in Figure 12.9.

12.2.6 COMPOSITING OF AIR SAMPLES

A method for compositing air samples collected from aeration tanks of an activated sludge tank has been reported.[21] This involves the use of a flux chamber equipped with a small outlet from which a measured volume of air sample is passed through a VOST containing adsorbent tubes. These are dual media adsorbent tubes containing 75 mg (4 cm long of 60/80 mesh Tenax TA) followed by 150 mg (4 cm long) Ambersorb KE 340, 1:1 volume.

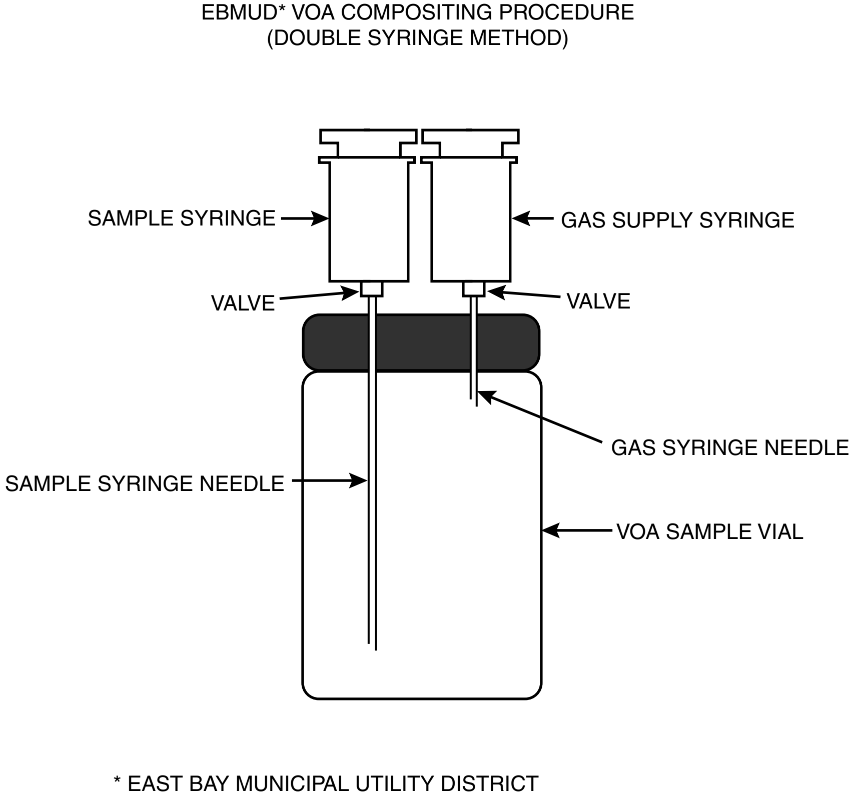


FIGURE 12.8 EBMUD* VOA compositing procedure (double syringe method).

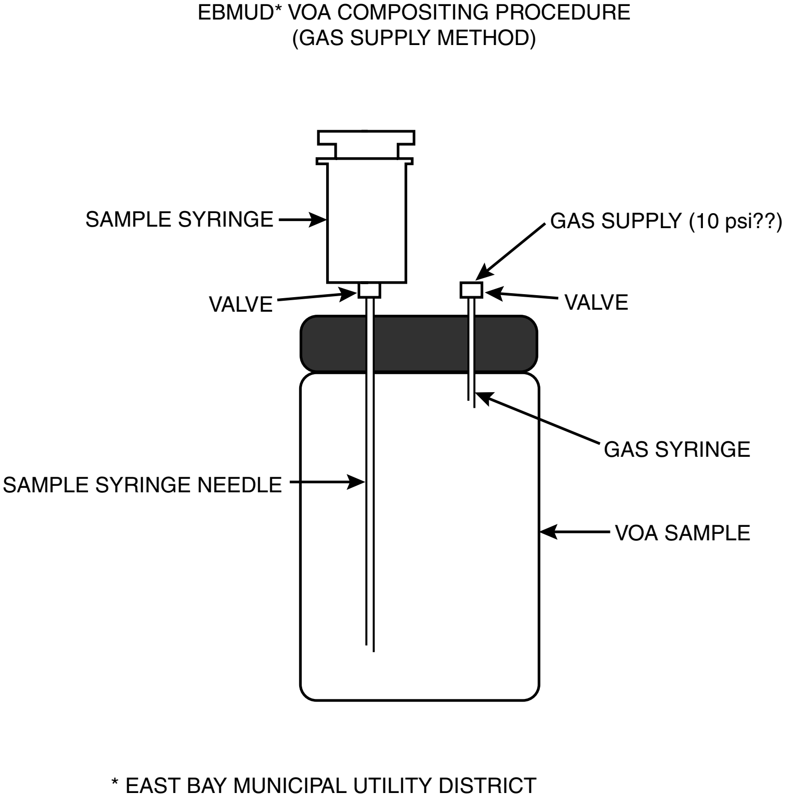


FIGURE 12.9 EBMUD* VOA compositing procedure (gas supply method).

Using this method of compositing, it was concluded that there was no statistically significant difference between the average VOC concentration arithmetically computed from the VOC concentration of individual grab samples and the VOC concentration of the composite sample made from these grab samples.

12.3 ANALYTICAL METHODOLOGY

Currently, only a few POTWs analyze for HAPs in air samples. Also, very few U.S. EPA-approved testing methods are used at the wastewater treatment plants for the analysis of the 188 HAPs. In some cases, state and local regulatory agencies have established only a few methods for the testing of air toxics. Therefore, for source testing and risk assessments, it is important to use either a published and approved method or an alternative such as a validated method in accordance with the U.S. EPA Method 301 validation procedures.

The VOHAPs are usually present at relatively low levels in different sample matrices. Therefore, the selection of a proper analytical method is essential for their determination. For instance, although GC/MS methods are suitable for screening the presence of a large number of VOCs, they are not considered sensitive for some analytes compared with methodologies using GC with multiple detectors. Some expert systems that guide the user in selecting appropriate GC detectors are available.

In GC methods, for example, SW-846 Method 8010 (for halogenated VOCs) and SW 846 Method 8020 (for aromatic VOCs), the method detection limits (MDLs) are usually <1 ppb (compared with MDLs of 1 to 5 ppb for GC/MS). However, GC methods require the use of a second column with a different mobile phase for confirmation and identifying interferences, whereas GC/MS confirms the presence of a compound through its molecular ion and fragmentation peaks.

In this section, an attempt is made to briefly describe recommended analytical methods for HAPs and for obtaining optimum detection limits for regulatory compliance by minimizing matrix effects. Standard Methods, SW-846 and various other texts provide detailed analytical methodologies. A quick review summary is also included in Table 12.2.

12.3.1 U.S. EPA METHOD TO-14

12.3.1.1 Scope and Application

The U.S. EPA Method TO-14 is suitable for analysis of volatile and semivolatile organic compounds from ambient and near-ambient air samples.[22] This method should not be used for samples collected from combustion sources.

12.3.1.2 Method Summary

The U.S. EPA Method TO-14 outlines the use of evacuated stainless canisters or Tedlar® bags for sample collection analysis by GC/MS. Volatile and semivolatile organic compounds from ambient air are cryogenically concentrated on sorbent traps and are then thermally desorbed into a capillary GC/MS system. This procedure is suitable for qualitative identification of gas-stream samples from POTWs from ambient or near-ambient sources such as scrubber ducts, flux chamber offgas and other noncombustion sources.[1] This method can use either GC with multiple detectors or MS in the selection ion mode (SIM) or scan mode or with an ion trap detector.

12.3.1.3 Interferences and Their Control

The Method TO-14 detection limits can be enhanced by using a suitable high-resolution GC and control of interferences. The MDL is usually at 0.5 to 1 ppb. Interferences may occur due to water vapor in the gas stream, which can be reduced by a nafion dryer, a second GC trap or by selection of a GC/MS with a differential pump. Dilution of the sample with a known amount during sample collection can also be done to maintain the moisture level in the canister below saturation. While this may result in higher MDLs, they still stay within ppt levels for halogenated and ppb levels for most other organic compounds.[19] The canister or bags must be properly cleaned before sample collection. Excessive levels of carbon dioxide present in a sample may interfere with the analysis by freezing up the cryogenic trap. A smaller aliquot of sample must be analyzed to avoid the error.

TABLE 12.2
HAP Instrumental Analysis Methods

Analytes	Analytical Method	Comments
VOC	U.S. EPA Method TO-14	Detection of VOC in ambient air using Summa canisters and GC/MD for low detection limits and GC/MS for full scan
VOC/Semi-VOC	U.S. EPA Method 18	Gaseous organics by GC from stationary sources
VOC	SW-846 Method 8260 B	Suitable for different matrices especially wastewater, sludges and solid waste
VOC	SW-846 Method 5041 A	Thermal desorption of sorbent cartridges from VOST (Method 0030) source sampling
BTX/Aromatic VOCs	SW-846 Method 8020	Detection of benzene, toluene, xylene from wastewater and combustion sources
Semi-VOC (base neutral/acid extractables)	SW-846 Method 8270	Suitable for different matrices especially wastewater, sludges and solid waste
Semi-VOC (base neutral acid extractables)	SW-846 Method 5041 A	Thermal desorption of sorbent cartridges from VOST (Method 0031) for source emissions
Formaldehyde, acetaldehyde, acrolein	CARB Method 430 or SW 846 Method 8315 A (Sampling method 0011)	Determination of aldehydes by HPLC of DNPH cartridges or midget impingers for stationary source emissions
Dioxins (PCDD & PCDFs)	SW-846 Method 8280 A	High-resolution GC/low-resolution MS using selective ion monitoring (SIM) technique for particulate and gaseous phase and liquid & solid waste
Dioxins (PCDD & PCDFs)	SW-846 Method 8290/ CARB 429	High-resolution GC/high-resolution MS for multimedia analysis
Polyaromatic aromatic hydrocarbons (PAH)	SW-846 Method 8100	A GC method for different matrices
Pesticides	SW-846 Method 8081A	Organochlorine pesticides by GC for soil and can be modified for air samples
Herbicides	SW-846 Method 8151A	Chlorinated herbicides in water and solid samples by GC methylation or pentafluorobenzylation determination
Polychlorinated biphenyls (PCBs)	SW-846 Method 8100, CARB 428	A GC method for different matrices

Cryogenic trapping or cryofocusing is another way to analyze HAPs, especially VOCs, found in various matrices. For instance, in a modified TO-14 method used by the City of Los Angeles' Air Testing Laboratory, Environmental Monitoring Division, air emissions from POTWs and landfills are detected in a modified Varian GC (Model 3600)-equipped PIDs and ELCDs. For detecting low levels of VOCs in the landfill migration gas or POTW open surfaces, the GC is equipped with a 100 mL loop and the sample is retained in the loop at –45°C for 9 minutes and then ramped to 240°C for desorption of analytes to capillary column by temperature programming. This procedure concentrates the low level analytes in the background air and can be detected at 0.5 to 1.0 ppb level. A similar method is also used by the SCAQMD and peer agencies.

12.3.2 U.S. EPA METHOD 18

12.3.2.1 Scope and Application

This method is used for the measurement of gaseous organic compound emissions by GC. This is the method most often recommended for measurement of organic compounds from combustion sources. However, it is not recommended for high molecular weight or very low boiling VOCs.[8]

12.3.2.2 Method Summary

For sampling, Tedlar® bags and adsorbent tubes are used. Canisters are not recommended by the U.S. EPA due to moisture interference. The method was modified in 1994, requiring the recovery of spikes to fall between 70 to 130% for samples collected in bags and adsorbent tubes.[23] No specific testing method has been identified with Method 18, but it requires a presurvey to develop and confirm the best sampling and analytical scheme. The analysis is usually done using a GC with a threshold MDL of 1 ppm or lower. To ensure better GC resolution and MDLs, it is recommended to optimize the GC conditions and proper purging of the sample loop by inert carrier gas.

12.3.2.3 Interferences and Their Control

Moisture interference can be minimized by using a proper dryer or correction factor by subtracting the amount of moisture.

12.3.3 SW 846 METHOD 8260 B

12.3.3.1 Scope and Application Method

8260 is used to determine VOCs in a variety of solid waste matrices. This method is applicable to nearly all types of samples at POTWs, regardless of water content, including various air sampling trapping media, aqueous sludges, mixed filter cakes, spent carbons, spent catalysts, soils and sediments. This method can be used to quantitate most of the VOCs that have boiling points below 200°C.

12.3.3.2 Method Summary

VOCs can be introduced into the GC/MS system by various techniques. Purge-and-trap (Methods 5030 for aqueous samples and 5035 for solid and waste oil samples) is the most commonly used. For air samples, Method 5041 provides methodology for desorbing volatile organics from trapping media (Methods 0010, 0030 and 0031). In addition, the direct analysis of these compounds can be performed by utilizing a sample loop for sub-sampling from Tedlar® bags (Method 0040).

The volatile compounds are then introduced into the gas chromatograph either directly to a wide-bore capillary column or cryofocused on a capillary precolumn before being flash evaporated to a narrow-bore capillary for analysis. The column is temperature-programmed to separate the analytes, which are then detected with an MS interfaced to the GC.

Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns can be directly interfaced to the ion source. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impactlike) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major ion relative to an internal standard using a five-point calibration curve.

12.3.3.3 Interferences and Their Control

Volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent cap are the major interferences. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided because such materials out-gas organic compounds, which will be concentrated in the trap during the purge operation.

Contamination may occur when a sample containing low concentrations of VOCs is analyzed immediately after a sample containing high concentrations of VOCs. A technique to prevent this problem is to rinse the purging apparatus and sample syringes twice with organic-free reagent water between samples.

Screening of the samples containing high concentrations of interfering compounds prior to the purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples.

Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, this will result in random background levels.

A trip blank should be prepared with organic-free reagent water and carried through the sampling and final analysis steps to check for contamination during the chain of custody and final analysis sequence.

Use of sensitive MS to achieve lower detection level will increase the potential to detect laboratory contaminants as interferences.

12.3.4 U.S. EPA METHOD 25 C

12.3.4.1 Scope and Application

Method 25C is used for measurement of total nonmethane organic compounds (NMOC) from stationary sources, POTWs or landfills.

12.3.4.2 Method Summary

The methane, carbon monoxide and carbon dioxide are removed by a GC column. The NMOCs are back-flushed from the head of the column, oxidized to CO_2, then eluted through a reducer that converts the NMOC to methane and detected with a GC equipped with a flame-ionization detector.

12.3.4.3 Interferences

Since whole air samples are collected in canisters, a high amount of CO_2 is present as a background interference.

12.3.5 SW-846 METHOD 8270 C

12.3.5.1 Scope and Application

Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media and water samples. Direct injection of a sample may be used in limited applications.

Method 8270 can be used to quantitate most neutral, acidic and basic organic compounds that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include PAHs, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds and phenols, including nitrophenols.

12.3.5.2 Method Summary

The samples are prepared for analysis by GC/MS using the appropriate sample preparation methodology described in SW-846 Method 3500 and, if necessary, sample cleanup procedures stated in SW-846 Method 3600.[6]

The sample extract containing the semivolatile organic compounds is injected into a GC with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a MS connected to the GC. The analytes eluted from the capillary column are introduced into the MS via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards. Quantitation is accomplished by comparing the response of a major ion relative to an internal standard using a five-port calibration curve.

12.3.5.3 Interferences and Their Control

Raw GC/MS data from all blanks, samples and spikes must be evaluated for interferences. A determination is made of whether the source of interference is in the preparation or cleanup of the samples and corrective action is taken to eliminate the problem.

Contamination by carry-over can occur whenever high- and low-concentration samples are sequentially analyzed. To reduce carry-over, the sample syringe must be rinsed with the solvent between sample injections. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross-contamination.

12.3.6 SW-846 METHOD 8280 A

12.3.6.1 Scope and Application

This method is appropriate for the detection and quantitation of 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (2,3,7,8-TCCD), 2,3,7,8-polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in water (at part-per-trillion concentrations), soil, fly ash and chemical waste samples, including still bottoms, fuel oil and sludge matrices (at part-per-billion concentrations). This procedure uses a matrix-specific extraction, analyte-specific cleanup and high-resolution (HR) capillary column GC/low-resolution (LR) MS (HRGC/LRMS) techniques. For part per trillion (ppt) to part per quadrillion (ppq) concentrations, high-resolution GC/HRMS can also be used, but at a relatively higher cost. If interferences are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination.

12.3.6.2 Method Summary

The analytical method requires the use of HRGC/LRMS on sample extracts that have been subjected to specified cleanup procedures. An aliquot of the concentrated extract is injected into an HRGC/LRMS system capable of performing the selected ion monitoring.

The identification of target compounds is based on their ordered elution and comparison to standard solutions from an appropriate GC column and MS identification. Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on a single column. The use of both DB-5 and SP2331 (or equivalent) columns is advised. No analyses can proceed unless all the criteria for retention times, peak identification, signal-to-noise and ion abundance ratios are met by the GC/MS system after the initial calibration and subsequent verification.

12.3.6.3 Interferences and Their Control

Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by running laboratory method blanks. The use of high-purity reagents and pesticide-grade solvents helps to minimize interference problems.

Interfering compounds coextracted from the sample will vary considerably from source to source, depending on the industrial process being sampled. PCDDs and PCDFs are often associated with other interfering chlorinated compounds such as PCBs and polychlorinated diphenyl ethers (PCDPEs), which may be found at concentrations several orders of magnitude higher than that of the analytes of interest. Retention times of target analytes must be verified using reference standards. Certain cleanup techniques may have to be implemented to achieve the sensitivity specified in this method.

High-resolution capillary columns are used to resolve as many isomers as possible; however, no single column is known to resolve all of the 210 isomers. The columns employed by the laboratory in these analyses must be capable of resolving all 17 of the 2,3,7,8-substituted PCDDs/PCDFs sufficiently to meet the method specifications.

12.3.7 CARB METHOD 429

12.3.7.1 Scope and Application

CARB Method 429 is used to determine PAH emissions from stationary sources.[19] The lowest MDL that can be achieved for a given sample by this method will depend on the types and concentrations of other chemical compounds contained in the sample, as well as the original sample size and instrument sensitivity.

The limitations on extension of the methodology to compounds other than the method target compounds are the availability of standards and the ability to perform chromatographic separations on vaporized compounds.

12.3.7.2 Method Summary

Particulate and gaseous phase PCDD/PCDF and PAH are isokinetically extracted from a stack and collected on an XAD-2 resin filter, in impingers and upstream sampling train components (Figure 12.10). The total amounts of PCDD/PCDF and PAH are determined by high-resolution GC/MS. It has not been demonstrated that the partitioning in the different parts of the sampling train is representative of the partitioning in the stack gas sample for particulate and gaseous PAH compounds.

The analytical method entails the addition of internal standards to all samples in known quantities, matrix-specific extraction of the sample with appropriate organic solvents, preliminary fractionation and cleanup of extracts (if necessary) and analysis of the processed extract for PAH using high-resolution capillary column GC coupled with either low- or high-resolution MS.

12.3.7.3 Interferences and Their Control

Modified U.S. EPA Method 5 sampling train can cause PAH transformation or formation of certain other products. The fact that PAHs can degrade or transform on sample filters is well documented. When trapped on filters, certain reactive PAHs such as benzo[a]pyrene, benzo[a]anthracene and fluoranthene can readily react with stack gases. Low levels of nitric acid and higher levels of nitrogen oxides, ozone, sulfur oxides have been known to react with these PAHs.

PAH degradation may be of a greater concern when they are trapped in the impingers. When stack gases such as sulfur oxides and nitrogen oxides come in contact with the impinger water, they are converted into sulfuric acid and nitric acid,

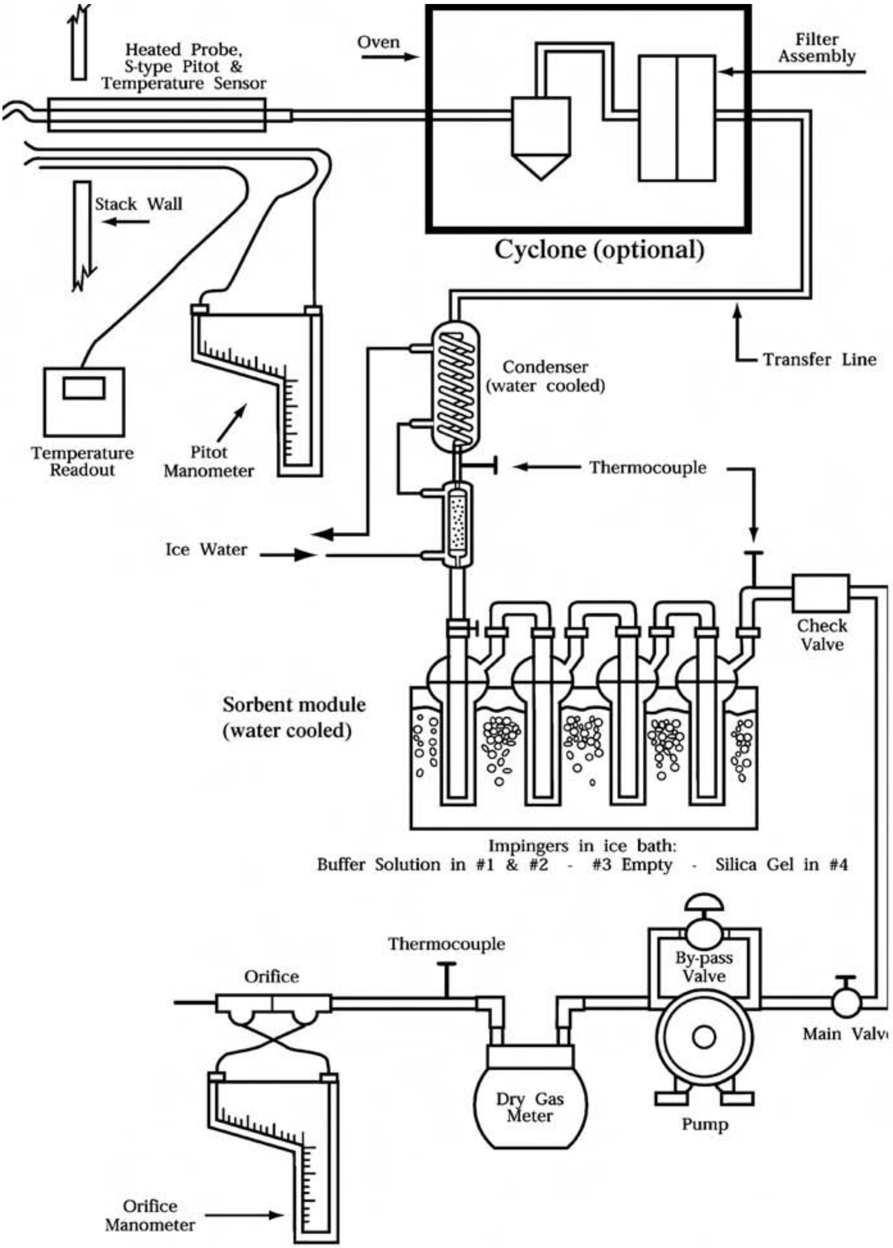


FIGURE 12.10 CARB 429 sampling train. (California Environmental Protection Agency, State of California Air Resources Board, CARB Method 429: Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions From Stationary Sources, Monitoring and Laboratory Division, Sacramento, California, Adopted: September 1989, Amended: July 1997.)

respectively. There is evidence that, under such conditions, certain PAHs will be degraded. It is recommended that the levels in the impingers be used as a qualitative tool to determine whether breakthrough has occurred in the resin.

To assess the effects of ozone, sulfur oxides and nitrogen oxides, the analyst should monitor concurrently for these gases during PAH sampling.

12.3.8 CARB METHOD 430

12.3.8.1 Scope and Application

CARB Method 430 (CARB 430) is used to determine formaldehyde and acetaldehyde emissions from stationary sources.[24]

12.3.8.2 Method Summary

To determine the concentration of aldehydes in a gas stream, gaseous emissions are passed through two midget impingers each containing aqueous acidic 2,4-dinitrophenylhydrazine (DNPH). They react with DNPH by nucleophilic addition on the carbonyl group followed by 1,2- elimination of water to form 2,4-DNPH derivatives. After extraction, the DNPH derivatives are determined by reverse phase high-performance liquid chromatography and ultraviolet (UV) adsorption detector. An instrument calibration check is performed for each run consisting of <20 samples using a control sample. The detection limit for formaldehyde is 8 ppbv, acetaldehyde 6 ppbv and other aldehydes 2 ppbv.

12.3.8.3 Interferences and Their Control

There appears to be a systematic error caused due to high levels of NO_2 interfering with the detection of formaldehyde when lean-burn engines are tested using CARB 430. Since CARB 430 does not specify volume of stack gas to be used, one solution would be that CARB comes up with a specific formula to adjust the sampling volume if the NO_2 levels are high.

12.3.8.4 Method CARB 430 vs. Fourier Transform Infrared (FTIR) Method

For last few years, U.S.EPA has been recommending use of the FTIR Method for the determination of formaldehyde emissions from reciprocal internal combustion engines (RICE). For instance, during the U.S. EPA's Industrial Combustion Coordinated Rulemaking (ICCR) program from 1996 to1998, RICE testing for formaldehyde was carried out using real-time monitoring and compliance methods. FTIR method was preferred since it has undergone the U.S. EPA Method 301 validation and results are consistent for different combustion devices including lean-burning RICE.

The CARB 430 uses the 2,4-DNPH colorimetric procedure to measure formaldehyde. The CARB 430 and the FTIR give satisfactory and comparative results for gas-fired boilers, heaters, turbines and rich-burning RICEs. The CARB 430 gives inconsistent and lower results with lean-burning RICE. The problem is that, when engine exhaust gas contains greater than 60 ppm of NO_2 (or mixture of NO plus oxygen), DNPH reagent reacts with excess NO_2 to form several derivatives. This derivative competes with DNPH-aldehyde reaction that can deplete the DNPH reagent (in a nonquantitative manner) resulting in a lower reading for formaldehyde.

Radian International carried out several studies for the Gas Research Institute (GRI), indicating that the above performance problem of CARB 430 procedure for internal combustion engine (ICE) in a laboratory study where different DNPH colorimetric procedures were compared with high content of NO_2 in the exhaust gas. In one of the studies, Radian adjusted the gas matrix to closely resemble the composition of the actual combustion exhaust gases (containing CH_4, CO, CO_2, NO, etc.).[25]

Recently, CARB provided the following recent developments on Method 430 in light of efforts to improve its performance in controlling interferences.[26]

1. In March, 2000, CARB started a feasibility study for improving and making CARB 430 applicable for the determination of acrolein in emissions of combustion sources. CARB 430 has never been validated for acrolein and is subject to severe acrolein interferences without further development. The CARB 430 is approved for formaldehyde and acetaldehyde only.
   CARB studied methods based on wet DNPH, dry DNPH (coated resin beads in glass cartridges), direct gas (canister) sampling and FTIR. Dry DNPH looked best for the determination of acrolein and improving the overall performance of CARB 430.
2. A review of the GRI study mentioned above shows that NO_x induces a bias and interferes in the determination of acrolein. CARB 430 also warns about interferences due to high moisture and particulate loading. However, it is also reported that better test performance was noticed as moisture rises, but below the dew point.
3. Per the CARB, interest in the feasibility study of CARB 430 for lean-burning ICEs and other combustion sources was too low to justify expenditure of resources. Instead, CARB issued an advisory letter regarding the use of Method 430 and the handling of its results. As a result, influential acrolein entries in tables of toxic emission factors have been deleted, most notably in the California Air Toxics Emission Factors (CATEF) tables.
4. Recently, interest has risen due to siting concerns regarding combined cycle turbines because of the California Energy Commission's interest in increasing utility load. Such sources present acrolein concerns. This may prompt further CARB 430 method development.

CARB also provided the following explanation regarding the "systematic error" when lean-burning engines are tested using CARB 430.

U.S. EPA Method 301 allows for the computation of a correction factor if some stringent statistical tests are passed. The correction factor is ± 10% of the adopted method value. Besides aldehyde concentrations, many other factors can affect CARB 430 results, especially in ICE exhaust. Some are difficult to quantify. Several derivatives formed can interfere with the determination of the analyte. Since nonquantitative measurements rarely yield systematic errors, the systematic error stated above could be quantitative only if it can be used to compute a correction factor per the U.S. EPA Method 301.

12.4 QUALITY ASSURANCE

While measuring for HAPs in any matrix, it is important to follow a sound quality assurance/quality control (QA/QC) protocol so that measurements are representative and can be replicated. Since most methods for the measurement of 188 HAPs are not validated by the U.S. EPA, it is important to conduct validation studies by using, for instance, Method 301. It is also recommended to use the U.S. EPA methods for federal regulatory studies whenever necessary, or to get the U.S. EPA perspective when using state or local district analytical methods. Recommended procedures for sample collection and handling are summarized below.

12.4.1 REPRESENTATIVENESS

The generation of quality data starts with the collection of representative samples. To ensure that the collected sample is representative, all aspects of the sampling program are planned and documented in detail. At a minimum, an acceptable sampling program should include the following:

- A proper statistical design that considers the goals of the study and its uncertainties
- Instructions for sample collection, labeling, preservation and transport to the analytical laboratory
- Training of personnel in the specified sampling techniques and procedures

12.4.2 Sample Integrity

To ensure sample integrity, the following elements are considered:

- Samples are collected according to the prescribed and approved written sampling standard operating protocols (SOPs).
- Samples are collected in appropriate containers.
- Sample containers are properly cleaned prior to use to ensure that the sample is not contaminated during the collection process.
- Appropriate volumes of samples are collected and preserved in a manner that minimizes the loss of target compounds.
- Samples are analyzed within their specific holding times.

12.4.3 Sample Chain-of-Custody

The chain-of-custody system is an essential element in assuring the future usefulness of measurement data. This system must provide a legally defensible record that originates with the assignment of sample containers, and provide an indication of all personnel involved with the samples, including the date and time of their involvement. The custody procedures must provide assurance that the integrity of the sample is maintained throughout the course of the collection, handling and analysis process. The custody procedures must minimize the opportunity for inadvertent contamination or intentional tampering with the samples.

12.4.4 Field Blanks and Duplicates

Periodically, a travel or trip blank, field blank or field sample duplicate may need to be collected. Specific guidelines provided in the SOPs should always be followed.

12.4.5 Sample Transport

Care is taken to ensure that the samples are not subjected to temperatures above ambient for any length of time to guard against thermal degradation of the analytes. Samples in Tedlar® bags are held in cardboard boxes to shield them from direct sunlight and potential damage during transport.

12.5 ANALYTICAL PROCEDURES AND CALIBRATION FREQUENCIES

12.5.1 Analytical Procedures

The Air Laboratory performs analyses using methods based on U.S. EPA, CARB or other approved methods such as those prescribed by SCAQMD methods. The SOP for each analysis includes a reference to the method being followed.

12.5.2 Laboratory Standards, Specialty Gases and Reagents

Calibration protocols require that an instrument demonstrate acceptable performance at the beginning of the analysis sequence and that the initial calibration is still valid after continued instrument operation.

12.5.3 Calibration Procedure and Frequency

Calibration of laboratory instruments must be performed according to the requirements of the analytical method, which are described in detail in the SOP for the analysis. All analytical instruments are subjected to initial calibration procedures. Calibration curves should have a minimum of three and typically five points and include a response factor for each analyte. Continuing calibration is demonstrated on a daily basis. The maximum time between demonstrations of continuing calibration is 12 h. The exact specifications for continuing calibration are as specified in the relevant U.S. EPA Method and typically require response factors to agree within 30% of the initial calibration value. In the event that continuing calibration cannot be demonstrated after corrective action (such as retuning instruments, maintenance of chromatographic columns, etc.), a new initial calibration curve should be generated.

12.5.4 Analytical Quality Control Samples

Several types of quality control samples are incorporated into each analysis to provide information on the performance of the method, instrument and possible matrix effects. The QC checks are specific to the analytical method and generally include the use of one or more of the QC samples such as initial and routine calibration standards, method blank and lab duplicate sample analysis.

12.6 METHOD DETECTION LIMITS AND REPORTING LEVELS

The most common definition of “detection limit” is the smallest amount that can be detected above the noise in a procedure within the stated confidence limit. The MDL is determined by processing the samples through the complete analytical method. Usually, seven analyses are conducted on aliquots of a solution containing the analyte of interest near the estimated MDL. The standard deviation (s.d.) of the seven analyses when multiplied by the one-sided t distribution for 6 degrees of freedom at 99% level (3.14) gives the desired MDL (MDL = 3.14 × s.d.). The MDLs may differ within laboratories due to the subjective variations in an analytical method. For reporting purposes, many laboratories prefer to use a practical quantitation limit (PQL). The PQL is the lowest level achievable among laboratories that can be used for reporting purpose with higher confidence than the MDL and allows detection within the precision limits established by the MDL determination. The use of the PQL is required by some regulators for reporting purposes and is usually estimated at five times the MDL.[5,19]

12.6.1 Achieving lower MDLs in Various Matrices

The importance of getting low MDLs of HAPs cannot be overemphasized in light of the drastic impact of high MDLs in emission estimates and resulting risk assessments. In Section 12.3 of this chapter, interferences that might impact MDLs have been addressed in specific methods. This section provides an overall view about various ways to lower the MDLs. The MDLs are directly proportional to the sensitivity of an analytical method, which, in turn, depends on the interferences due to the sample matrix and presence of interfering compounds in the blank. Matrix is a component or substrate containing the analytes of interest. Per SW-846 guidelines, quality control measures such as the inclusion of a matrix spike, spike duplicate and selection and use of surrogates for organic methods should be used to address matrix spike bias and precision. When the concentration of an analyte in the sample is >0.1%, no spike is necessary. For overriding the matrix effects, MDLs for specific matrices should be determined.

For detecting low levels of VOCs, care should be taken to avoid contamination through synthetic organics such as phthalates in plastic labware and gloves, and in chemicals used in lubricants and greases. Use of polytetrafluoroethylene (PTFE)-coated plastic tubing and sealants is recommended to address this problem. In addition, organic solvents such as hexane, acetone, ether and methylene chloride used for extraction and concentration of semivolatiles, PCBs and pesticides may be present in the laboratory air and may interfere with the detection of VOCs from air samples. According to the U.S. EPA guidelines in SW-846 for sampling method for VOCs (Method 0031), if high levels of hydrocarbons are present in the emission matrix, preliminary screening of samples with distributive volumes may be necessary. This will enable the analyst to determine the volume of sample where matrix interference impacts the concentration of VOCs of interest and a saturation of the analytical instrument may occur. This approach can also be used during sampling as well as analyses. A similar technique, method of standard addition, is used to address the interfering matrices during atomic absorption spectrophotometric analysis of metals. To perform sampling according to distributive volumes, sample volumes are collected or analyzed in increasing concentrations (100 mL, 200 mL, 300 mL) to verify the corresponding change in analyte concentration (1×, 2×, 3×).

12.6.2 GUIDELINES FOR REPORTING DATA BELOW DETECTION LEVELS FOR RISK MANAGEMENT AND POTENTIAL HEALTH RISK ASSESSMENTS (HRAs)

Some guidelines need to be followed in assessing health risks associated with HAPs that are found at near detection limits or below detection limits in gaseous emissions. Although a HAP is absent in a given sample, sometimes it is assumed that the HAP is present at a concentration equal to half the MDL. If such is the case, the risk is elevated, although none readily exists.

The achievement of the MDLs or zero standard might not be practical, cost-effective, or even prudent. Compliance or legal standards are usually determined according to the health risks involved, whereas detection limits are based upon the limitations of the analytical instrumentation. Advancement in analytical instrumentation has enabled detection limits to be lowered to ppb or ppt levels; sometimes these are well below the legal standards. However, air toxics not detected are assumed to be at the detection limit value or half the detection level for purpose of HRA quantification. In the latter case, it is important to follow some reasonable guidelines to assess the risk associated with nondetected compounds with reasonable accuracy without unduly inflating the risk. This could result in the installation of costly control equipment and requirement to report HAPs even after they have been controlled, reduced or were nonexistent to begin with.

To resolve this issue, some regulators recommend the back calculation of MDLs using risk-screening techniques. When the necessary MDL has been determined, the source testing methods can be adjusted as necessary to meet the limit, such as by increasing the sample collection time. This procedure is recommended in California under AB 2588 Air Toxics "Hot Spots" Information and Assessment Act of 1987 and ensuing CAPCOA 1990 guidelines for HRAs.[27]

The SCAQMD has published procedures for determining the emission estimates to be used in risk assessments for nondetected compounds in analyses using methods approved by the agency. These procedures provide methods for estimating the most likely emission levels of nondetected compounds based on consideration of the likelihood of the presence and MDLs of such HAPs. In addition, procedures are included for excluding such compounds from risk assessments. The SCAQMD provided new guidelines for estimating emissions of nondetected toxic air contaminants (TACs) and using blanks in emission estimations for the purpose of preparing HRAs required under Rules 1401 and 1402.[28, 29] For a HAP or TAC to be excluded from testing or use in HRA, it must meet either of the following three screening conditions:

1. No likelihood of the presence of a TAC
2. Absence of a TAC or its precursors in the process
3. Any TAC listed in Special TAC list developed for POTWs.

If a TAC does not pass the initial screening guidelines, the facility must quantify and report the emissions of the compound through the appropriate air quality management district (AQMD)-approved test methods and guidelines. Three possible scenarios discussed in the guidelines for quantifying TAC emissions are as follows:

1. If TACs in all source test runs are below the limit of detection (LOD), the compounds can be identified as nondetected and no HRA is needed.
2. If a TAC is detected in less than 10% of the test runs, then for those TACs below the LOD in these runs, a zero value will be used. Averages of the measured values obtained for the TACs greater than LOD along with zero value for the TACs below LOD in other runs will be used to report the final average result.
3. When a TAC is detected in 10% or more of the test runs, then one half of the LOD for the TACs is assigned in those runs where TACs were detected below LOD. An average of the measured values is obtained for the runs with TACs that were above LOD and with half LOD values for TACs in the runs below LOD. The final average result is reported and used for the HRA.

A guidance document by U.S. EPA Region III addresses quality and consistency of handling of the data near the detection limit in conducting HRAs.[30] As a regional document it was meant to clarify and augment some areas in the national U.S. EPA documents since none presents a procedure for assessing risks from undetected compounds.[31, 32] The aforementioned document recommends a "decision path" for the risk assessors. The decision path involves criteria such as presence of a compound at hazardous level (resulting in one in one million risk), or a compound occurring at down-gradient level to a detected chemical, physical/chemical characteristic of the compound and the impact of using half the detection limit for nondetected compounds on route-specific risk estimates.

During the compliance for California's AB 2588,[2] Los Angeles used the following methodology for assessing compounds detected below MDLs at its POTWs. This approach was taken after the consultant CH2M HILL discussed the issue with

CARB and the SCAQMD and accepted an approach taken by the Bay Area AQMD and the Sacramento Metropolitan AQMD.[2]

In instances where a TAC is detected in any air sample from a liquid process, but not detected in the liquid phase, one half the detection limit was used for the liquid sample. When a nondetect occurs in both media, a zero value is used (this did not occur). In instances where a compound was found in the liquid phase but was not detected in the air phase, a zero value was used. This decision path was considered acceptable since the air flow rates are relatively lower at POTW point and nonpoint sources (2000 to 35,000 scfm) and, with low detection limits of VOCs, the mass emission rate in case of benzene was 1 lb/year — well below the *de minimis* levels specified in AB 2588.

12.7 PERSPECTIVE AND CONNECTIVITY

12.7.1 USE OF DIRECT ASSESSMENT TECHNIQUES FOR RISK ASSESSMENT

The SCAQMD regulations such as Rules 1179, 1401, 1402 and AB 2588 require emission inventories or emission estimates for risk assessments. For instance, SCAQMD in its Rule 1179[3] required POTW operators to submit VOCs and odor emission inventories. The rule either allowed direct source testing or the following emission estimation methods:

- Mass balance using empirical factors
- Emission model such as BASTE
- PEEP
- Historical data from the plant and other POTWs

The emission rate estimates made through air modeling may have a high degree of uncertainty due to meteorological conditions and site-specific variability, and because POTWs receive and treat a diverse array of HAPs received from domestic and unregulated sources. In that event, direct source testing is the most effective technique to quantify emissions from POTWs. However, the cost could be prohibitive. The U.S. EPA is also trying to address the issue of addressing ambiguity of HAP emissions at POTWs.[7] For this, the U.S. EPA is resorting to use of its WATER8 model, which is one of the more conservative air models.[33] However, air models are typically very conservative and a POTW could be classified as a major source of HAP emission's triggering strict regulations. AMSA submitted a position paper on POTW MACT to U.S. EPA in November 1998,[34] where it expressed its preference to using direct source testing for determining a major source status. In addition, AMSA also requested that alternative air models such as BASTE and TOXCHEM+ be also allowed for determining the emission rates of VOCs. The U.S. EPA published the National Emission Standards for Hazardous Air Pollutants (NESHAPs) for Publicly Owned Treatment Works on October 26, 1999. It developed a flexible methodology to determine if a POTW is a major source.[35]

To address this problem, several municipal agencies are proactively developing target lists of compounds for quantification, compliance monitoring, reporting and risk assessment purposes. For instance, the City of Los Angeles developed a reduced list of 13 VOCs for its POTWs for AB 2588 compliance. This list was based on the historical influent data and GC/MS scan data of field samples collected by the consultant CH2M HILL from representative POTWs including the City of Los Angeles. For combustion sources, aldehydes, PAH, PCBs, heavy metals and a few other compounds were added based on the data from other similar combustion sources from POTWs. It has been the City of Los Angeles's experience that direct source tests give more accurate results than other estimation methods.[1]

In 2001, SCAQMD approved a TAC short list of about 50 compounds for POTWs for testing and determination of health risk associated with the air emissions from liquid phase, sludge treatment processes and combustion processes under risk assessment procedures for Rules 1401 and 1402. The TAC short list was developed by the Southern California Association of POTWs (SCAP) from over 300 compounds listed in the amended Rules 1401 and 1402. It was based on the PEEP under the AB2588 emissions inventory program, the JEIP under Rule 1179 inventory and TACs that have a likelihood of being present in the air emissions of POTWs.

12.7.2 TRADITIONAL AND PERFORMANCE-BASED REGULATORY COMPLIANCE MONITORING

The purpose of emission monitoring is either to demonstrate compliance with the established regulatory limit or to evaluate or assess an environmental risk assessment. In some cases, a pretest estimate of the permissible risk determines the target concentration for stationary source emissions. Federal, state and local air district regulations require the use of specific "prescribed" sampling and analytical procedures for compliance monitoring. The agencies that allow alternate test procedures (ATPs) require elaborate and even cumbersome approval procedures from the U.S. EPA regional administrator (for wastewater methods), or a designee of the administrator (for drinking water and air methods), or the executive officer for the local air district approved methods.

Due to advances in analytical measurement technology, the regulatory methods fail to meet the rigors of the advanced instruments in detecting new constituents at lower detection levels. Recognizing these issues, the U.S. EPA started to consider a performance based monitoring system (PBMS) to allow the regulated community to use new or emerging technologies to meet the regulatory limits. Beginning in 1996, the U.S. EPA's approach shifted from requiring specific procedures for measurement to specifying project-specific performance criteria for selecting a suitable measurement method in a cost-effective manner. In May 1996, the PBMS was adopted by the U.S. EPA. The revisions to CFR Parts 60, 61 and 62 will entail referencing to the existing test methods as an option and performance criteria (data and measurement quality objectives, DQO and MQO) as an alternative option.

The adoption of the PBMS approach represents a fundamental shift from the traditional processes that the U.S. EPA has used to approve new or alternative monitoring methods. This new approach imposes legal accountability for the achievement of specific data and measurement quality objectives without requiring the particular procedures, techniques or instrumentation for achieving such objectives. The emphasis would be on how to document data quality rather than on gathering data. While the PBMS offers analytical flexibility, it incorporates critical performance criteria to assure analytical performance. The exceptions to the PBMS approach will be specific test parameters defined by a method such as the toxicity characteristic leaching procedure (TCLP) or, when it is expensive, to use an alternative reference method. The PBMS system intends to provide measurement flexibility by allowing regulated community to resolve interferences and find low-cost field measurement alternatives.

12.8 SUMMARY

Effective sampling and analytical methods are critical components of POTW efforts to develop an accurate inventory and to quantify air toxics emissions required for developing regulatory compliance strategies. A variety of sampling procedures are available for HAPs and depend on the emission source: liquids, solids or air (ambient or near-ambient) generic samples, and point source or combustion [or a combination of various source types). Currently, only a few POTWs analyze for HAPs in air samples and very few regulatory-approved testing methods are available. Therefore, for source testing and risk assessments, it is important to use either a published or approved method or a method that follows U.S. EPA validation procedures.

While measuring for HAPs in any matrix, it is important to follow a sound QA/QC method for sample collection and handling so that measurements are representative and can be replicated. Careful analytical procedures and accurate calibration frequencies are also important.

California's SCAQMD has established regulations requiring emission inventories or emission estimates for risk assessments. In addition to direct source testing, several emission estimation methods are allowed — mass balance using empirical factors, emission model, PEEP emission factors and historical data. Several municipal agencies are proactively developing target lists of compounds for quantification, compliance monitoring, reporting and risk assessment purposes.

Advances in analytical measurement technology have moved forward more quickly than regulatory requirements for detection levels. In recognition of these issues, the U.S. EPA has started to consider a PBMS approach to allow POTWs to use new or emerging technologies to meet regulatory limits.

ACKNOWLEDGMENTS

We gratefully acknowledge Dr. Vlad Kogan (County Sanitation Districts of Orange County, Fountain Valley, California), Dr. Paul Pau (Department of Water & Power, City of Los Angeles), and Dr. Dariush Vosooghi (Plant Operations, Bureau of Sanitation, City of Los Angeles) for technical review of the manuscript. We also thank Cindy Castronovo (California Air Resources Board, Sacramento) for providing technical review of CARB diagrams.

REFERENCES

1. California Assembly Bill 2588 (AB 2588) Air Toxics "Hot Spots" Information and Assessment Act of 1987, Air Toxics Program, Sampling and Analytical Methods, Hyperion Treatment Plant, City of Los Angeles, Vol. 2 and Final Report, Hyperion Treatment Plant, City of Los Angeles, Vol. 4, August 1990.
2. South Coast Air Quality Management District (SCAQMD), Rule 1179.
3. South Coast Air Quality Management District (SCAQMD), Rule 1401.
4. South Coast Air Quality Management District (SCAQMD), Rule 1402.
5. American Public Health Association, American Water Works Association and Water Environment Federation, *Standard Methods for the Examination of Water and Wastewater,* 18th ed., 1992.
6. U.S. EPA, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, 3rd ed., Publication No. SW-846, Office of Solid Waste & Emergency Response, Washington D.C., 1996.
7. U.S. EPA, National Emission Standards for Hazardous Air Pollutants: Publicly Owned Treatment Works, Research Triangle Park, NC: 40 CFR Part 63, 230, 66084-66101, 1998.
8. U.S. EPA, Method 18: Measurement of gaseous organic compound emissions from stationary sources, *Code of Federal Regulations, Title 40, Part 60*, Appendix A, Washington D.C., Office of the Federal Register, 1987, (modified April 22, 1994).
9. ASTM, *Standards on Environmental Sampling, Standard Test Method for Determination of Volatile Organic Chemicals in Atmospheres, Canister Sampling Methodology*, D 5466-95, 775–793, 2nd ed., 1997.
10. Entech Instruments, Inc., Canister Cleaning System, Model 3100, Simi Valley, California.
11. California Environmental Protection Agency, State of California Air Resources Board, CARB Method 422, Stationary Source Test Methods, Determination of VOCs in Emissions from Stationary Sources, Monitoring and Laboratory Division, Sacramento, California, Amended Dec. 1991.
12. Schmidt, C.E., Theory and operation of the U.S. EPA Surface Emission Isolation Flux Chamber at POTWs. One-day training course for Bureau of Sanitation, City of Los Angeles, July 11, 1994.
13. Schmidt, C.E., *Sampling and Analysis of Airborne Pollutants*, E.D. Winegar and L.W. Keith, (Eds.), Ch. 3, 1993.
14. Jiang, J. et al. The development of a sampling system for the determination of odor emission rates from area surfaces: I. Aerodynamic performance, *J. Air Waste Mgmnt Assoc.*, 45, 917, 1995.
15. Jiang, J. and Kaye, R. The selection of air velocity inside a portable wind tunnel system using odor complaint database, *Proc. Water Environment Federation's Odors/VOCs Specialty Conference,* Houston, 1997.
16. Witherspoon, J. et al. Theoretical and practical considerations in the use of wind tunnels for odor emissions measurement, *Proc. Water Environment Federation's Odors and Toxic Air Emissions Specialty Conference,* Albuquerque, New Mexico, 2002.
17. American Conference of Governmental Industrial Hygienists (ACGIH), *Advances in Air Sampling*, 1989.
18. Keith, L.H. and Walker, M.W., *Handbook of Air Toxics, Sampling, Analysis and Properties*, Lewis Publishers, Boca Raton, 1995.

19. California Environmental Protection Agency, State of California Air Resources Board, CARB Method 429: Determination of Polycyclic Aromatic Hydrocarbon (PAH) Emissions From Stationary Sources, Monitoring and Laboratory Division, Sacramento, California, Adopted: September 1989, Amended: July, 1997.
20. Campbell, L., Radian International, memo to Carl Loos (Shell Oil) on TO-14 sampling protocol, July 211997.
21. Moschandreas, D.J., Basu, S. and Tata, P., Compositing and storage of air and wastewater samples, *J. Env. Eng.*, 360–371, April 1999.
22. U.S. EPA, Compendium of Methods for Determination of Toxic Compounds in Ambient Air (EPA-600/4-89-017 and Supplements: 600/4-87-006, 600/4-87-013), Research Triangle Park, North Carolina, 1989.
23. Dishkijian, R., U.S. EPA, Method 18 news bulletin, Emission Measurement Center, (undated).
24. California Air Protection Agency, State of California Air Resources Board, CARB Method 430: Stationary Source Test Methods, Volume III, Methods of Determining Toxic Air Contaminants from Stationary Sources, Monitoring and Laboratory Division, Sacramento, California, Sept. 1989.
25. McCarthy, J., FTIR vs. CARB Method 430, Personal communication and presentation made at the U.S. EPA's Integrated Coordinated Combustion Rulemaking (ICCR) meeting by Testing/Monitoring group of the ICCR Committee, Nov. 8, 1996.
26. Loop, J., California Air Resources Board, Personal Communication on CARB Method 430, Aug. 1 2000.
27. Erbes, R., *A Practical Guide to Air Quality Compliance*, 2nd ed., John Wiley & Sons, New York, Ch. 5, 1996.
28. South Coast Air Quality Management District (SCAQMD), Risk assessment procedures for rules 1401 and 212, Version 5.0, Diamond Bar, California (undated).
29. South Coast Air Quality Management District (SCAQMD), Personal communication with Steve Barbosa, Principal Chemist, July 19, 2000.
30. U.S. EPA, Region III Guidance on Handling Chemical Concentration Data Near the Detection Limit in Risk Assessments, (Smith, R.L. Ed.), Nov. 4, 1991.
31. U.S. EPA, Guidance for Data Usability in Risk Assessment *(DURA),* EPA/540/G-90/008, 1990.
32. U.S. EPA, *Risk Assessment Guidance for Superfund (RAGS), Vol. 1, Human Health Evaluation Manual (Part A)*, EPA/501/1-89/002, 1989.
33. U.S. EPA, *User's Guide for Wastewater Treatment Compound Processor and Air Emissions Estimator (WATER 8)*, Research Triangle Park, North Carolina, Nov. 1984; EPA-453/C-94-080C and WATER 8, Version 3.0, 1995.
34. Association of Metropolitan Sewerage Agencies (AMSA), Position paper on U.S. EPA's proposed MACT Rule for POTWs, 1998.
35. U.S. EPA, National emission standards for hazardous air pollutants: publicly owned treatment works, *Federal Register*, 64(206), 57572-57585, 1999.

13 VOC Emission Estimation Methods

Prakasam Tata and Jay Witherspoon

CONTENTS

13.1 Introduction 258
13.2 Conservative Mass Balance 259
13.3 Conservative Mass Balance with Adjustments 259
13.4 Flow-Related Emission Factors 259
13.5 Concentration-Based Emission Factors 260
  13.5.1 Pooled Emission Estimates Program (PEEP) Factors 260
    13.5.1.1 Covered and Ducted Liquid Process Emission Factors ... 263
    13.5.1.2 Uncovered Liquid Processes: Quiescent Surfaces 263
    13.5.1.3 Uncovered Liquid Processes: Diffused Air Activated Sludge Process 264
    13.5.1.4 Combustion Processes 264
    13.5.1.5 Weirs 265
    13.5.1.6 Sludge Drying Beds 266
    13.5.1.7 Digester Gas VOC Emissions 267
  13.5.2 Joint Emissions Inventory Program (JEIP) Emission Factors 267
    13.5.2.1 Liquid and Semisolid Unit Processes 267
    13.5.2.2 Combustion Sources 269
  13.5.3 TriTAC Emission Factors 269
13.6 General Fate Models 269
  13.6.1 Collection Systems 270
    13.6.1.1 AP-42 Emission Factors 270
    13.6.1.2 BACT/LEAR Model Emission Factors 270
    13.6.1.3 BASTE Model 270
    13.6.1.4 CORAL+ Model 271
    13.6.1.5 TOXCHEM+ Model 272
    13.6.1.6 WATER8/9 Model 272
    13.6.1.7 SEAM (Secondary Emission Assessment Model) 273
    13.6.1.8 naUTilus Model 273
  13.6.2 Wastewater Treatment Systems 273
    13.6.2.1 WATER8/9 274

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

13.6.2.2 TOXCHEM/(+) 275
13.6.2.3 BASTE 275
13.6.2.4 CINCI 276
13.6.2.5 NCASI 276
13.6.2.6 TORONTO 276
13.6.2.7 PAVE 276
13.6.2.8 EPA FATE 277
13.7 Source Testing 277
13.7.1 Confined Sources 277
13.7.2 Unconfined Sources 278
13.8 Tracer Method 278
13.9 Summary 279
References 279

13.1 INTRODUCTION

To respond to the pending Clean Air Act Amendments (CAAA) of 1990, industries and municipal agencies in the late 1980s and early 1990s increased efforts to determine the magnitude of the VOC emissions from their collection systems and wastewater treatment units. The objective was to determine whether a particular entity was a "major" source of VOC emissions and to identify appropriate technologies to control the VOC emissions of a source if it was found to be a major source.

The determination of VOC emissions from POTW unit processes and collection systems is complex, difficult and costly. Difficulties associated with the determination of VOC emission rates include:

- Temporal variability in the VOC concentration of POTW influents i.e., from shift-to-shift within a day, day-to-day, diurnal and seasonal
- Unavailability of reliable analytical methods with very low detection limits (such methods are needed because of the low concentration of VOCs found in wastewater influents and air)
- Significant variability in the detection limits of VOCs present in the in influent, effluent, sludges and air (due to this variability it is difficult to get accurate material balances)
- Cost associated with sampling and analyses of VOCs
- Lack of suitable compositing techniques to pool samples for minimizing cost and variability in the data gathered

Due to these difficulties, most emission estimate determinations resort to the use of emission factors, models and default estimates.

A few different methods exist for estimating the VOC emissions from POTWs and industrial sources. These methods are based on approaches such as mass balance, derivation of emission factors, modeling and tracer techniques. These are as follows:[1–5]

- Conservative mass balance
  - Conservative mass balance with adjustments
  - Flow related emission factors
  - Concentration-based emission factors
- PEEP factors
- JEIP factors
- Tri-TAC factors
  - General fate models
- Collection systems
- Wastewater treatment systems
  - Source testing
- Confined sources
  - Unconfined sources
- VOC tracer method

13.2 CONSERVATIVE MASS BALANCE

This emission estimation methodology takes a simplistic approach. The difference between the influent VOC load to a POTW and the VOC load leaving the POTW via the effluent is assumed to be the VOC mass lost due to volatilization. Obviously, this is a very crude approximation of the volatilization losses of the VOCs, as many are known to be biologically degraded as well as sorbed to sludge solids. Also, such emission estimates reflect plantwide emissions encompassing many unit processes. These estimates cannot yield emission estimates for individual unit processes. Chang, Schroeder and Corsi[6] were among the first few to make such an approach in a study that they conducted in California to obtain approximate VOC emission estimates. A similar approach was made by Noll and De Paul[7] to obtain a conservative estimate of the VOC emissions from the seven water reclamation plants owned and operated by the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC).

13.3 CONSERVATIVE MASS BALANCE WITH ADJUSTMENTS

This method of VOC estimations is similar to the one above, except it adjusts the influent and effluent concentration from a unit process with an emission or adjustment factor that accounts for sorption or biodegradation. Also, an emission factor may be applied to the product of the influent VOC concentration and flow. The associated emission factors are also derived for many of the combustion sources using such an approach.

13.4 FLOW-RELATED EMISSION FACTORS

These are the simplest, as they require only the volumetric flow to a unit process. Emissions are calculated as shown in Equation 13.1 (TriTAC[2]):

$$\text{Daily emissions (lbs/d)} = \text{unit process flow (mgd)} \times \text{emission factor (lbs/d/mgd)} \tag{13.1}$$

These factors can be refined according to the influent characteristics (residential or industrial) and differences in operational parameters between the facility from which the emission factor is obtained and the facility for which an estimate is required. The results from this approach are conservative and can be obtained at a reasonable cost.

13.5 CONCENTRATION-BASED EMISSION FACTORS

Concentration-based emission factors are derived in California in programs conducted by a consortia of POTWs. These programs were carried out in response to the state regulatory initiative to control VOC emissions. Concentration-based emission factors are superior to flow-based emission factors because they are related to the measured influent pollutant loading of the individual treatment process.[2] Emission factors derived under the PEEP, JEIP and TriTAC programs conducted in California are discussed below.

13.5.1 Pooled Emission Estimates Program (PEEP) Factors

As previously discussed, PEEP was created when 25 public agencies formed a joint powers agreement to develop emission factors at a cost of $2.5 million over an 11-month period under a contract with the James M. Montgomery Consulting Engineers, Pasadena, California, for compounds and processes specific to wastewater treatment facilities. The PEEP emission factors were derived by using approved sampling and analytical protocols for various VOCs for 18 wastewater unit treatment processes. This effort included the collection of 2060 air and 1220 liquid and sludge samples from 20 POTWs. These facilities had flow range of 3 to 380 mgd and a combined total flow of 1576 mgd.

Table 13.1 presents the treatment plants, their design flows and the various unit processes investigated in the PEEP study to obtain the emission factors.[3]

The following 25 VOCs were analyzed: acetaldehyde; acrolein; benzene; 1,3-butadiene; carbon tetrachloride (tetrachloromethane); chloroform (trichloromethane); p-dichloro-benzene (1,4-dichlorobenzene); 1,4-dioxane; ethylene dibromide (1,2-dibromomethane); ethylene dichloride (1,2-dichloroethane); ethylene glycol monoethyl ether; ethylene glycol monoethyl ether acetate; ethylene glycol monomethyl ether; ethylene glycol monomethyl ether acetate; formaldehyde; methyl chloroform (1,1,1-trichlorethane); methylene chloride (dichloromethane); perchloroethylene (tetrachloroethene); styrene, (20) toluene; trichloroethylene; trichlorofluoromethane; vinyl chloride; vinylidene chloride (1,1-dichloroethane); xylenes.

The approach taken for deriving the emission factors for various unit processes is based on the VOC concentration of the influent to a given unit process. Emission factors were derived for covered and ducted liquid processes, uncovered liquid processes, combustion processes, weirs and others.

TABLE 13.1
Unit Processes from Which Emission Factors Were Derived in the PEEP Study at Different Wastewater Treatment Plants[3]

Unit Process		Treatment Plants	Flow, mgd
Aerated grit chamber	1.	Joint Water Pollution Control Plant, County Sanitation Districts of Los Angeles County	380
	2.	County Sanitation Districts of Orange County, Plant No.1	60
	3.	Encina Water Pollution Control Facility	19
Primary Sedimentation Tanks	1.	South Bayside System Authority Wastewater Treatment Plant	21
	2.	County Sanitation Districts of Orange County, Plant No.1	60
	3.	Union Sanitary District of Alvarado Wastewater Treatment Plant	23
Diffused air Activated Sludge	1.	Union Sanitary District of Alvarado Wastewater Treatment Plant	23
	2.	County Sanitation Districts of Orange County, Plant No.1	60
	3.	Encina Water Pollution Control Facility	19
Mechanically aerated facilities	1.	City of Corona, Wastewater Treatment Plant 2	3
Pure oxygen activated Sludge	1.	Joint Water Pollution Control Plant, County Sanitation Districts of Los Angeles County	380
	2.	Sacramento Regional Wastewater Treatment Plant	135
	3.	East Bay Municipal Utility District	85
Trickling filter	1.	Fairfield-Suisun Sewer District	14
	2.	Delta Diablo Sanitation District	10
Secondary clarifier	1.	Joint Water Pollution Control Plant, County Sanitation Districts of Los Angeles County	380
	2.	County Sanitation Districts of Orange County, Plant No.1	60
	3.	Encina Water Pollution Control Facility	19
Tertiary filter	1.	South Bayside System Authority Wastewater Treatment Plant	21
	2.	County Sanitation Districts of Orange County, Plant No.1	60
	3.	Fairfield-Suisun Sewer District	14
Chlorine contact tank	1.	Chino Basin Municipal Water District, RP1	32
	2.	San Jose Creek Reclamation Plant, County Sanitation Districts of Los Angeles County	63
	3.	Las Virgenes Municipal Water District Tapia Water Reclamation Plant	10
	4.	Chino Basin Municipal Water District, RP2	7
	5.	Irvine Ranch Municipal Water District Water Reclamation Plant	5
	6.	City of Riverside Water Quality Control Plant	32

TABLE 13.1 (CONTINUED)
Unit Processes from Which Emission Factors Were Derived in the PEEP Study at Different Wastewater Treatment Plants[3]

Unit Process		Treatment Plants	Flow, mgd
Dechlorination Facilities	1.	South Bayside System Authority Wastewater Treatment Plant	21
	2.	San Jose Creek Reclamation Plant, County Sanitation Districts of Los Angeles County	63
	3.	San Francisco Southeast Water Pollution Control Plant	72
Dissolved air flotation Thickeners	1.	Joint Water Pollution Control Plant, County Sanitation Districts of Los Angeles County	380
	2.	County Sanitation Districts of Orange County, Plant No.1	60
	3.	Sacramento Regional Wastewater Treatment Plant	135
Gravity Thickeners	1.	South Bayside System Authority Wastewater Treatment Plant	21
	2.	Union Sanitary District Alvarado Wastewater Treatment Plant	23
Anaerobic digesters	1.	Joint Water Pollution Control Plant, County Sanitation Districts of Los Angeles County	380
	2.	County Sanitation Districts of Orange County, Plant No.1	60
	3.	Eastbay Municipal Utility District	85
Internal combustion Engines	1.	Joint Water Pollution Control Plant, County Sanitation Districts of Los Angeles County — 1100 hp Ingersoll Rand	380
	2.	County Sanitation Districts of Orange County, Plant No.1-1500 hp Delaval DGSR-36	60
	3.	County Sanitation Districts of Orange County, Plant No.2 — 375 hp	200
	4.	County Sanitation Districts of Orange County, Plant No.2 — 160 hp Climax MSP # 10	200
	5.	County Sanitation Districts of Orange County, Plant No.2 — 320 hp Waulesha MSP # 6	200
	6.	Chino Basin Municipal Water District RP1 — 827 hp Waukesha	32
	7.	Chino Basin Municipal Water District RP1 — 525 hp Waukesha	32
	8.	Palm Springs Water Pollution Control Facility — Caterpillar	
	9.	Palm Springs Water Pollution Control Facility — 75 hp Waukesha	
Boilers	1.	Joint Water Pollution Control Plant, County Sanitation Districts of Los Angeles County	380
	2.	County Sanitation Districts of Orange County, Plant No.1	60
	3.	East Bay Municipal Utility District	85
Belt filters	1.	County Sanitation Districts of Orange County, Plant No.1	60
	2.	County Sanitation Districts of Orange County, Plant No.2	200

TABLE 13.1 (CONTINUED)
Unit Processes from Which Emission Factors Were Derived in the PEEP Study at Different Wastewater Treatment Plants[3]

Unit Process		Treatment Plants	Flow, mgd
Centrifuges	1.	Joint Water Pollution Control Plant, County Sanitation Districts of Los Angeles County	380
	2.	City of Los Angeles, Hyperion Treatment Plant	380
	3.	East Bay Municipal Utility District	85
Sludge Drying Beds	1.	San Bernardino Water Reclamation Plant	25

Source: James M. Montgomery Consulting Engineers Inc., PEEP (Joint Powers Agencies for Pooled Emission Estimation Program) Final Report for Publicly Owned Treatment Works (POTWs), Pasadena, California, 1990.

13.5.1.1 Covered and Ducted Liquid Process Emission Factors

The emission factor for these processes (e.g., incinerators, head works and chlorine contact tanks, if ducted) is computed as the fraction of the total mass of VOC of the influent liquid stream removed from the unit due to volatilization. It is expressed below as Equation 13.2:

$$\mathrm{EF} = \frac{\mathrm{E}}{\mathrm{ML}} \tag{13.2}$$

where

E = rate of air emission = (Q air out × C air out) − (Q air in × C air in) Q and C are flow rate and concentrations of air and pollutant

ML = mass loading of VOC = Q (liquid in) × C (liquid in) Q and C are the flow rate and concentration of the pollutant

13.5.1.2 Uncovered Liquid Processes: Quiescent Surfaces

It is difficult, if not impossible, to obtain the air flow rate and emissions flux leaving the open surface of the treatment unit process. Floating flux chambers or hoods having a surface area of 8.75 ft^2 are used to collect the emissions from quiescent tanks or activated sludge aeration tanks.[8–11] For quiescent basins, air containing a target VOC at a certain concentration is supplied from a gas cylinder at a flow rate to achieve at least two air changes under the hood per hour. Air emission, E, is calculated as shown in Equation 13.3:

$$\mathrm{E} = \frac{\mathrm{A}}{8.75}(\mathrm{Q\ hood.})\ (\mathrm{C\ hood.out} - \mathrm{C\ hood.in}) \tag{13.3}$$

where

Q = volume of hood

C (hood.in) and C. (hood.out) = concentration of the pollutant in the air from the gas cylinder entering the hood and the concentration of the pollutant leaving the hood and A = the total surface area of the tank for which emission rate is calculated.

The “E” value (Equation 13.3) is then substituted for “E” in Equation 13.2 to obtain the emission factor for the unit process.

13.5.1.3 Uncovered Liquid Processes: Diffused Air Activated Sludge Process

As adequate air containing any contaminants escapes from the surface of aeration tanks, the air emission from the process can be calculated as shown in Equation 13.4:

$$E = \frac{A}{8.75}(\text{Q hood.})\,(\text{C hood.out} - \text{C air.in}) \qquad (13.4)$$

where

C air.in = concentration of VOCs of in air.in

C hood.out = concentration of VOCs in the air.out

This equation can be then substituted for “E” in Equation 13.2 to obtain the emission rate for the diffused air activated sludge unit.

13.5.1.4 Combustion Processes

The mass loading of a pollutant to combustion devices, such as engines, boilers, etc., using digester gas as the fuel, should take into account the total amount of pollutant present in the digester gas, inlet air and other influent streams. It is given by Equation 13.5:

$$\text{ML} = (\text{Q dig.gas.in} \times \text{C di.gas.in}) \times \text{Q air.in} \times \text{C air.in}) \qquad (13.5)$$

The air supplied is likely to contain a high concentration of pollutants and should be monitored. Since these are removed in boilers, accurate measurements of airflow rates is needed to obtain organic removal credits.

Emissions load in the exhaust gases is calculated as before and shown in Equation 13.6:

$$E = \text{Q exhaust air} \times \text{C exhaust air} \qquad (13.6)$$

As airflow rate to combustion devices is not usually metered, argon concentrations in the digester gas, inlet air and exhaust air are measured. The air supplied to the unit can be calculated provided the digester gas flow rate is known, The value of ML was then calculated using Equation 13.5. The emission factor EF is then calculated as the ratio of E:ML.

13.5.1.5 Weirs

Emission factors for weirs are calculated based on a mass balance approach. The difference in the influent and the effluent contaminant load amounts to "E"

$$E = (Q\ \text{inf} \times C\ \text{inf}) - (Q\ \text{eff} \times C\ \text{eff}) \qquad (13.7)$$

Insertion of Equation 13.7 into Equation 13.2 yields the "EF"; ML is equal to Q inf × C inf.

Apart from the above simplistic approach to determine emission factors for weirs, the PEEP study[3] determined emission factors based on the VOC deficit ratio, which is correlated with the oxygen deficit ratio by Pincince[12] as follows. It may be recalled that the VOC deficit ratio, r_v and oxygen deficit ratio, $r_{o,}$ (D_u/D_d VOC) are related as shown in Equation 13.8:

$$r_v = (C_u\,\text{VOC}/C_d\,\text{VOC}) \qquad (13.8)$$

where

C_u and C_d are upstream and downstream VOC concentrations of a weir

$$r_o = (D_u / D_d) \qquad (13.9)$$

where,

D_u and D_d are upstream and downstream oxygen deficit ratios of a weir

$$\text{Ln}\,(r_v) = \text{Ln}\,(r_o)\,[KL_v / KL_o] \qquad (13.10)$$

where

KL_v and KL_o are VOC and oxygen mass transfer coefficients per h.

Conversion of Equation 13.10 from the above format to the $\log_{10}$ format, it can be written as:

$$r_v = r_{o,}\Psi \qquad (13.11)$$

Roberts, Munz and Dandliker[13] determined Ψ to be 0.67 ± 0.06 for many organics. To use Equation 13.11 with source test data analysis a relationship between this equation and the computed emission factors (EF) needs to be developed. This is done as follows. Based on a mass balance approach, the VOC emissions are assumed to be the difference between the VOC mass upstream of a weir and the VOC mass downstream of a weir and can be represented as shown in Equation 13.12:

$$\text{Air emissions} = Qcu_{VOC} - Qcd_{VOC}, \tag{13.12}$$

where

Q is the flow rate of wastewater entering and leaving the weir and
cu_{VOC} and cd_{VOC} are upstream and downstream VOC concentrations, i.e., Qcu_{VOC} is mass loading entering the weir and Qcd_{VOC} is the mass loading leaving the weir

Emission factors are represented as before;

$$EF = E \text{ (air emissions)} \div ML \text{ (Mass loading of VOCs entering weir)} \tag{13.13}$$

Therefore,

$$EF = E \text{ (air emissions)} \div Qcu_{VOC} \tag{13.14}$$

Referring to Equation 13.8, where r_v, is the VOC deficit ratio, the emission factor, EF, can then be related to the difference in the upstream and downstream weir VOC concentrations as shown in Equation 13.15:

$$\begin{aligned} EF &= (Q\,C_u\,VOC - Q\,C_d\,VOC) \div Q\,C_u\,VOC = 1 - [C_d\,VOC \div C_u\,VOC] \\ &= 1 - [1/r_v] \end{aligned} \tag{13.15}$$

The EF can then be related to the oxygen deficit ratio as follows:

$$EF = 1\text{-}[\,1\,/\,r_o\Psi] \tag{13.16}$$

13.5.1.6 Sludge Drying Beds

Equation 13.4 can be used to determine the emissions from sludge drying beds using a flux chamber. A known volume of sweep air is passed over the sludge surface under the hood for a certain time period. The emission rate is computed after getting the data from several experimental runs. A weighted average emission rate that can be converted to a daily or monthly rate is then obtained. The initial VOC loading rate is computed from the sludge volume placed under the hood and its corresponding VOC concentration. The emission factor is computed as the total mass emission of the VOC divided by the VOC mass loading in the sludge. However, the use of a single emission factor developed from a single sludge drying area to estimate the emissions from other sludge drying areas located at other municipal agencies is risky, because such factors may not truly reflect the emissions from these areas. It is prudent to estimate VOC emissions based on several site-specific measurements made under different environmental and climatic conditions rather than depending on emission factors developed elsewhere under unknown conditions.

13.5.1.7 Digester Gas VOC Emissions

VOCs contained in digester feed may also be contained in the digester gas produced. In addition, other VOCs that are otherwise not present in the digester feed may be formed during anaerobic digestion. The emission factor can be derived from the VOC concentrations of digester feed and the digester gas. The mass of VOCs contained in digester feed and the mass of VOCs contained in the digester gas can be computed as follows:

$$\begin{aligned} ML &= Q(\text{digester feed}) \times C(\text{digester feed}) \\ E &= Q(\text{digester gas}) \times C(\text{digester gas}) \end{aligned}$$

The computed numbers of ML and E can be substituted in Equation 13.2 to get the emission factor EF.

PEEP emission factors were rated A through E. The A rating was given to emission factors developed based on 10 or more direct source measurements at different plants. The poorest rating was E, given to emission factors based on a single observation of questionable quality or computed based on extrapolating an emission factor obtained from a similar process elsewhere.

Each emission factor reported in the PEEP study is the median value of three to nine source tests from the same unit process. These measurements were conducted at one to seven separate test sites. A summary of these emission factors, how they compare with emission factors in other studies and a discussion on the use of these emission factors for screening and regulatory purposes are presented in Chapter 14.

13.5.2 JOINT EMISSIONS INVENTORY PROGRAM (JEIP) EMISSION FACTORS

13.5.2.1 Liquid and Semisolid Unit Processes

SCAQMD Rule 1179 promulgated in 1991 stipulated that POTWs with a flow of >10 mgd must submit VOC and odor emission inventories. Twelve JEIP agencies operating 22 POTWs undertook the task. One of the objectives of this program was to develop emission factors for 16 standard unit processes:

1. Primary sedimentation tanks
2. Flow equalization tanks (primary effluent and secondary effluent)
3. Diffused air activated sludge
4. Mechanical activated sludge
5. TFs
6. Secondary clarifiers
7. Gravity filtration
8. Chlorination
9. Final effluent discharge weir
10. Final effluent evaporation ponds
11. DAF

12. Sludge dewatering centrifuges
13. Belt press sludge dewatering
14. Sludge conveyor
15. Storage sludge cake
16. Sludge trucking

Emission factors were derived by using two approaches: (1) a mass balance approach method and (2) field-testing to obtain directly measured values of VOC concentrations in air samples and the corresponding VOC concentration of the influent entering the unit processes.

The mass balance approach is highly conservative. It assumes that the difference between the VOC concentrations of the influent and effluent of a unit process are all due to volatilization. This may at times yield negative mass balances due to variability in samples and method detection limits of the analytical methods used on the influent and effluent samples from a unit process. The emission factors are calculated as follows:

$$\begin{aligned}\text{EF (lb/yr)} = {} & \text{mass of VOCs entering the inlet of the unit process (lb/year)} - \\ & \text{mass of VOCs leaving the unit process (lb/year)}\end{aligned}$$

In the direct measurement approach, emission factors were computed for uncontrolled emission locations (i.e., prior to treatment by an emission control technology device, fugitive emissions, or vent stacks). These were computed by dividing the mass of directly measured VOCs from a specific unit by the mass of VOCs entering via the wastewater into the unit process. Thus, the emission factor of a unit process is expressed as follows:

$$\begin{aligned}\text{EF} = {} & \text{VOC emissions to the air (directly measured, lb/year)} \div \\ & \text{VOC mass entering the unit (lb/year)}\end{aligned}$$

Emission factors can also be computed by a similar approach for controlled emission locations. These estimated emissions, which reflect the emissions actually discharged to the ambient environment, can further be corrected by deducting the VOCs present as background concentration in the ambient air environment.

For facilities where direct measurements of VOCs are not made, the annual emission rate can be computed for a unit process as follows, using the emission factors developed elsewhere for similar units:

$$\begin{aligned}\text{lbs of VOCs emitted/yr} = {} & \text{VOC mass entering the unit/year} \times \\ & \text{EF of a similar unit at another site}\end{aligned}$$

The average values of the JEIP emission factors and their ranges are presented in Chapter 14.

13.5.2.2 Combustion Sources

JEIP emission factors for combustion sources were also developed using direct measurement techniques. However, VOC emissions were estimated by using available emission factors and annual plant or combustion source fuel usage at the JEIP agencies. These values are given in Chapter 14.

13.5.3 TRITAC EMISSION FACTORS

This program is jointly sponsored by the League of California Cities, California Association of Sanitation Agencies and California Water Pollution Control Association (now known as the California Water Environment Association). In this program, VOC emission factors were derived by both the concentration and flow-based approaches.

concentration-based daily emissions (lb/d) = flow to unit (mgd) × pollutant concentration (lb/mgd) × emission factor (lb emitted/lb in the liquid influent)
flow-based daily emissions (lb/d) = unit process flow (mgd) × emission factor (lb/d/mgd)

The concentration-based method requires the collection of data on pollutant loadings derived by actual flow and VOC concentration in the influent flow, whereas the flow-based method requires only the flow to the treatment unit and a factor that is developed for it. In the Tri TAC study, emission factors were developed for total VOCs as well as individual species of VOCs. The total VOCs were determined by using U.S. EPA Method 25.2.

13.6 GENERAL FATE MODELS

Public domain as well as proprietary models are available for estimating VOC emissions from POTW collection systems and treatment unit processes. Differences exist in the models developed, although they have the same objective of predicting a reliable and accurate estimate of VOC emissions. The differences lie in the degree of site-specific data needed, default data and the extent of the treatment by different pollutant pathways, i.e., volatilization, sorption, biodegradation, photolysis, etc. VOC losses due to abiotic reactions such as photolysis are generally considered negligible. An important aspect of any modeling effort is to use input data of good quality. Such data can only be obtained by using analytical and sampling techniques that have undergone extremely rigid validated QA/QC protocols.

A brief description of the models currently available for modeling VOC emissions from collection and wastewater treatment systems is given below. The authors do not endorse a given model(s). A municipal agency wishing to obtain its own VOC estimates is advised to become familiar in advance with what a model can or cannot achieve, its underlying assumptions and its degree of reliability before an effort is made to obtain the estimates.

13.6.1 COLLECTION SYSTEMS

The following approaches and models are available for estimating VOC emissions from collection systems.[2,14-17]

AP-42 Emission Factors
BACT/LAER Document Emission Factors
BASTE model
CORAL/CORAL+
WATER8/WATER9 models
SEAM and TOXCHEM+
TOXCHEM+
naUTilus Model

13.6.1.1 AP-42 Emission Factors

The use of U.S. EPA's AP-42 emission factors is the easiest and simplest method for estimating VOC emissions from industrial sewers. For example, an emission of 0.07 lb of VOCs per hour is given per drain. This number is multiplied by the number of drains in a collection system to obtain the total mass emission of VOCs per hour.[16] This approach obviously assumes that all drains emit the same quantity of VOCs/hr and that the influence of neither the temperature nor any other characteristic of the drain has any effect on the volatilization rate. Thus, the approach of using emission factors is empirical and can be used for screening and planning purposes in an industrial setting and is perhaps overly conservative for municipal sewers. For further information: U.S. EPA website: www.epa.gov/ttn/chief.

13.6.1.2 BACT/LEAR Model Emission Factors

These factors are obtained in a U.S. EPA study that addressed industrial sewer emissions.[18] The approach is based on using emission factors and takes into account the effects of air and wastewater flow rates. The Henry's Law constant is the only impacting parameter for VOC losses. The characteristics of sewers are considered. Some assumptions made in this approach are:

- The sewers are half full.
- Flow in the channel for estimating fractional emissions is 80% of the design depth.
- The concentration of the exiting air is in equilibrium with the VOC concentration in the wastewater.
- The wind speed is 3.5 mph.[19]

For further information: U.S. EPA website: www.epa.gov/ttn/chief.

13.6.1.3 BASTE Model

In this model, only drop structures of sewerage systems are considered. Henry's Law coefficient for 26 VOCs and sewer parameters, such as drop height and width, tailwater depth, wastewater flow rate, influent VOC concentration, wastewater temperature and wind speed were considered. The upstream and downstream dissolved oxygen concentrations of a sewer drop provide the oxygen deficit ratio, which then is used to determine the VOC deficit ratio. This deficit ratio in turn determines the VOC loss between the upstream and downstream of a sewer drop, enabling the computation of VOC emissions as previously discussed.

The BASTE model requires the input of a measured ventilation rate, which is a serious limitation in the use of the model when these rate values are not available. The features of the BASTE model are further discussed elsewhere in Section 13.6.2. For further information: CH2M HILL, Oakland, California.

13.6.1.4 CORAL+ Model

This model[20] predicts sewer VOC emissions from drop structures and open and closed sewer reaches, which are considered as a series of continuously stirred tank reactors both in the liquid and gaseous phases. The model can only estimate emissions from a single sewer reach or drop structure. Hence, for multiple sewer reaches, estimates have to be made individually, taking the relevant conditions into consideration. The model, which can estimate VOC emissions for continuous and dynamic discharges, is menu driven and has a large database of VOCs with their physicochemical characteristics. VOC emissions from drop structures are estimated based on the oxygen deficit ratio of the upstream and downstream dissolved oxygen concentrations as developed by Nakasone[21] and by extrapolating this ratio to the VOC deficit ratio as in the BASTE model. However, in contrast to the BASTE model, the CORAL model accounts for gas phase resistance to mass transfer. Thus, the fundamental assumption in this model is one of nonequilibrium between the VOC concentration in the liquid and gaseous phases. Hence, the VOC losses are guided by the mass transfer between the gaseous and liquid phases and the ventilation rate between the sewer and its ambient environment. Such a mass transfer can be significant if air entrainment of VOCs is dominant. Lower VOC emission estimates can result when mass transfer principles are assumed in contrast to the assumptions based on equilibrium of the VOC concentration between the gaseous and liquid phases. The estimated emission rates may be significantly different from the actually measured emission rates. Like the BASTE model, the CORAL model is limited in its application due to the lack of measured sewer ventilation rates. Also, it does not take into account other competing factors such as adsorption and biodegradation. Biodegradation can be a significant factor in sewers, particularly in those where sewage takes a long time to travel to reach a POTW for treatment. If such is the case, the estimated emissions will be much higher than the actual emissions.

The input parameters for this model to estimate closed reach emissions are flow rate of the wastewater, upstream wastewater VOC concentration, ambient air VOC concentration, temperature of the wastewater, length and diameter of the sewer reach, slope and roughness coefficient and ventilation rate. Additional parameters are needed for estimating VOC emissions from closed drop structures. These are drop height, drop air or water flow ratio (i.e., ventilation rate), drop tailwater depth and drop gas volume. The model was evaluated by Corsi, Chang and Schroeder[20] under field conditions using a tracer (deuterated chloroform, $CDCl_3$) and it overpredicted, on an average, the experimental values by 28%. Emissions of other VOCS that are highly biodegradable, unlike $CDCl_3$, may be overpredicted to an even greater degree. This model was reported to predict VOC emission rates from drop structures with a predicted to measured stripping efficiency of 0.99 in field and pilot-scale experiments.[22] However, simulation results with this model also suggest that VOC emissions are highly sensitive to wastewater flow rate; they increase as the flow rate decreases. It is beneficial if industries are encouraged by municipal agencies to discharge during nights for the purpose of flow equalization and reducing VOC emissions.[23] For further information: Enviromega Inc., Dundas, Ontario, Canada; www.environmega.com/index.htm.

13.6.1.5 TOXCHEM+ Model

This model uses an algorithm similar to the CORAL+ model. Unlike the CORAL+ model, it can predict VOC emission rates from multiple sewer reaches. Also, unlike the CORAL+ model, it has no option for dynamic simulation of VOC discharges for estimating emissions. Emissions from process drains are estimated in a manner similar to the WATER8 model. TOXCHEM also does not account for other VOC fate pathways (i.e., biodegradation and adsorption). However, it has a large database of compounds. Air ventilation rates need to be provided by the user of the model. For further information: Enviromega Inc., Dundas, Ontario, Canada; www.environmega.com/index.htm.

13.6.1.6 WATER8/9 Model

Unlike the BASTE and CORAL+ models, the prediction of VOC emissions by the WATER8/9 models from closed collection system elements, such as closed lift stations, is based on the assumption of equilibrium of VOC concentration between the gaseous and liquid phase, rather than on mass transfer phenomena. On the contrary, these BASTE/CORAL models predict emissions from open collection system units, such as reach manholes, based on mass transfer phenomena. The primary mechanism of VOC losses is by volatilization. The required inputs to the models are: (1) wastewater velocity and flow rate, (2) reach width and length, (3) opening area of manholes, (4) air velocity through manhole openings, (5) upstream wastewater VOC concentration, (6) ambient air and water temperatures, (7) wind speed and (8) oil content of wastewater. These models provide default values of ventilation velocity. Using these values in conjunction with the dimensions of the opening in the collection system will allow the model to compute the ventilation rate as the product of these two values. If site-specific data are available, they should be used. The oil content of the wastewater is a model input parameter that enables the model to take into account the partitioning of VOCs into the oil and biomass fractions. (See also the discussion on naUTilus model below.) Because of the assumption that equilibrium exists between oil and wastewater, the model tends to overestimate when oil floats and presents itself on top of the wastewater. The mass transfer models employed by CORAL+ and WATER8/9 models can yield widely different VOC emission rates from sewer reaches. These models also do not account for adsorption and biodegradation that might occur in sewer reaches.

13.6.1.7 SEAM (Secondary Emission Assessment Model)

This model, developed by Enviromega Inc., calculates the VOC losses from drains, drop structures and sewer reaches. The sewer reaches, as in the CORAL+ model, are modeled as a series of CSTRs, and volatilization is assumed to be driven by nonequilibrium conditions. Other components of the sewer collection system included in this model are process drains, water seals, open and closed reaches, open and closed drop structures, lift stations and air treatment devices. User inputs to the model include the requirement of a reach by a specified number of CSTRs, various sewer elements and other parameters involving mass transfer phenomena. The model is based on a materials balance approach and incorporates correlation of mass transfer that is previously published.[21,24,25] SEAM is limited by the lack of a ventilation calculation. A value for the ratio of the flow rate of gas (Q_G) and flow rate of liquid (Q_L) must be input to perform the computation of ventilation rate. A selection of improper values will result in erroneous emission rates. The model also requires each drain to have a nonzero inflow.

SEAM is integrated as a subcomponent of the TOXCHEM+ model used for the prediction of fate of VOCs in wastewater and collection treatment system. For further information: Enviromega Inc., Dundas, Ontario, Canada; www.environmega.com/index.htm.

13.6.1.8 naUTilus Model

This model was developed by Dr. Richard Corsi and his associates David Olson and Sunil Varma at the University of Texas, Austin. It allows estimation of VOC emissions from entire industrial sewer networks from the point of discharge of a waste from specific units called “inside the battery limit (ISBL)” and through the main collection system termed “outside the battery limit (OSBL).” This model can also be used for municipal sewers. The model is based on a consideration of fundamental mass transfer kinetics, fluid dynamics and heat transfer principles to determine air exchange rates between the sewer and ambient air. It is integrated as a subcomponent of the WATER9 model.

Recently, the naUTilus model has been linked with the Global Geographic Information Systems (GIS) technology through the ArcView® software package to predict the stripping efficiency and VOC emissions from large industrial collection systems under varying flow, environmental and sewer conditions, such as changes in flow rates, temperature, wind speed, number of sealed drains, ventilation pattern etc.[16] For further information: U.S. EPA website: www.epa.gov/ttn/chief.

13.6.2 WASTEWATER TREATMENT SYSTEMS

Baillod et al.,[26] having compared the salient features of these models and delineated the differences among them, expressed that, ideally, a fate model should be:

- Conceptually correct.
- Realistic.
- Complete.
- Able to access and estimate toxicant properties.
- Modular, i.e., the model should be able to simulate a wastewater treatment plant with its constituent process units and associated flow regimes.
- Versatile, i.e., the model should be able to simulate the operational and design attributes.
- User friendly.

These are very high expectations and the currently available models fall short of them.

Various VOC general fate models have been developed for predicting VOC fate and emissions from wastewater treatment systems. Some of them can model for wastewater treatment unit processes only. Others can model a combination of wastewater treatment unit processes and collection systems. Some models are available in the public domain, whereas others are proprietary. A general description and a comparison of the general fate models are given here. A comparison of the results obtained with three of the models, USEPA8, BASTE and TOXCHEM/(+), which are widely used by wastewater professionals and accepted by regulatory agencies, is presented in Chapter 14.

The following are the models described in the literature that predict VOC emissions from collection or wastewater treatment plants: WATER8/9, TOXCHEM+, BASTE, CINCI, NCASI, TORONTO, PAVE and EPA FATE

13.6.2.1 WATER8/9

These are public domain U.S. EPA models, the WATER9 model being the latest upgrade of the previous versions of WATER8 and WATER7. They are designed to predict VOC emissions from wastewater collection and treatment unit processes. WATER8 is a DOS-based model, contains a database of more than 950 compounds and identifies up to 20 compounds from the master compound database. Using the UNIFAC method, it can also estimate properties of compounds that are not listed in the database.

WATER9 is a Windows-based program. It has access to over 2000 compounds and their properties. It can identify up to 100 compounds from the master compound database. It also has an updated database with an extensive list of compound properties from the Design Institute for Physical Properties (DIPPR) 911 database. A database of the Syracuse Research Corporation known as SMILECAS is also included. Using these databases, it is possible to obtain information on the structure and Chemical Abstracts Service (CAS) numbers of more than 100,000 compounds. This model accepts input parameters specified by the modeler or uses the needed parameters of specific compounds that are automatically estimated. It can adjust for the effects of temperature, multiple phase partitioning and pH.

Wastewater treatment units that can be modeled include bar screens, DAF or grit removal tanks, open trenches, mix tanks, primary clarifiers, equalization basins, trickling filter, cooling tower with biological activity, aerobic biological treatment (mechanical surface aeration, subsurface diffused aeration, high-purity oxygen aeration), API or oil–water separators, storage tanks, oil film units and oil press separators, lagoons, waterfalls, effluent unit etc.

WATER9 has a total of 49 process units, including collection systems, treatment units and some units that may be added to a treatment facility in the future. VOC emissions can be predicted from other unit processes such as biofilters, landfills, land treatment etc., by the WATER9 model. Equations used in simulating the various fate mechanisms for this model are given elsewhere.

13.6.2.2 TOXCHEM/(+)

This proprietary model was developed by Enviromega Inc., Dundas, Ontario. The model includes 204 chemicals in its database and simulates both the collection and treatment portions of a wastewater treatment system. It simulates the customary wastewater treatment unit processes as in WATER8/9 and BASTE. The model allows for predicting the fate of organic compounds under steady state or dynamic conditions and allows for back-calculating contaminant loads that can be allowed into a treatment plant at its head end. The model can use both the metric and U.S. units. TOXCHEM+ and its recent version 3 simulate both the collection and treatment system of a wastewater treatment facility. This recent version can be linked to an online supervisory control and data acquisition (SCADA) system to receive signals from flow meters, suspended solids and temperature sensors to model online the fate of contaminants. While the earlier version of the TOXCHEM model simulated biodegradation based on the first order reaction rate, the more recent version included the Monod kinetics function. Also, some additional units such as biological gas cleaning, trickling filter and cooling towers are added. It is also accepted by various state agencies to address regulatory issues pertaining to air emissions.

13.6.2.3 BASTE

This proprietary model was developed by the Bay Area Air Toxics Group (BAAT) by CH2M HILL[27] with Dr. Richard Corsi, University of Texas, Austin. It operates in a Windows-based environment and allows for flexibility in simulating a wide variety of treatment processes only. It can simulate only drop structures and not other units in collection systems. It can simulate aerated and nonaerated conveyance channels connecting unit processes, grit chambers, primary settling tanks, weirs completely mixed and plug flow air-activated sludge and high-purity oxygen reactors, trickling filters and secondary settling tanks. It can be used in the designing process when new facilities are built. It is useful in predicting what effects that process modifications will probably have on air emissions. Thus, it can be used for evaluating various control technologies. It has only 26 compounds in its database, but can model additional compounds for which the requisite properties, i.e., physical, chemical and biochemical, are known. Equations used in simulating the various fate mechanisms are given for this model elsewhere. It is accepted by various state regulatory agencies for addressing air emission issues.

13.6.2.4 CINCI

This is an integrated public domain model developed by Govind, Lai and Dobbs[28] of the University of Cincinnati and U.S. EPA to predict the fate of VOCs in wastewater treatment systems. The model includes the physical, chemical and biochemical properties of 196 chemicals. There is some capability of including other compounds based on the derivation of their properties according to quality structure activity relationships (QSAR). The essential mechanisms of volatilization, sorption and biodegradation are included. Process units that can be simulated include primary treatment followed by secondary treatment with returned sludge recycle and secondary treatment with and without sludge recycle. This model is not widely used because of its limited capabilities.

13.6.2.5 NCASI

This public domain model was developed by Barton[29] for the National Council of the Paper Industry for Air and Stream Improvement, Inc (NCASI). The purpose of the model was to predict VOC emission from the treatment process only. Its database includes physical properties of only 11 chemicals. Henry's Law constants, sorption and diffusion coefficients and biodegradation constants are given for nine chemicals. All the important VOC fate mechanisms are simulated. This model can simulate the secondary treatment portion of a wastewater treatment system as a completely mixed reactor along with the secondary clarifier as a unit. This model is not widely used because of its limited abilities.

13.6.2.6 TORONTO

This model, developed in Canada by Clark et al.,[30] can be obtained from the Ministry of the Environment. It can simulate the primary sedimentation and activated sludge treatment processes. There are 18 chemicals in its database and the basic VOC fate mechanisms are included in the model. Henry's Law coefficients, sorption coefficients and biodegradation constants are given in the database for these compounds. This is a relatively simple model and uses a fugacity approach for determining the solubility of the organic chemicals. This approach assumes that the conditions of equilibrium of a compound existing in the air–wastewater interface are a function of the fugacity of the compound. The model simulates grit chambers, primary settling tanks, aeration basins of an activated sludge process and secondary clarifiers. It is not widely used because of questionable assumptions, e.g., lack of validation on full-scale systems and limited abilities.

13.6.2.7 PAVE

Three separate emission models are available as part of the Programs to Assess Volatile Emissions (PAVE) package, namely, Surface, Subsurface and Spoils and Spills. The Chemical Manufacturers Association developed this package. Two of the models, Surface and Subsurface, represent steady state aerated basin emission wastewater treatment plants (either with or without biodegradation). Both the surface-aerated and diffused air-activated sludge systems can be simulated by this program. The third model, Spills, simulates liquid mixture emissions from nonaerated pools, such as tanks, equalization basins and nonflowing pools. It is not widely used by municipal agencies. Schroy[31] compared this model with BASTE, TOXCHEM and WATER7 and concluded that the PAVE model predicted the most accurate effluent VOC concentrations. However, the PAVE model predicted somewhat higher air emissions than those predicted by WATER7 and TOXCHEM models.

13.6.2.8 EPA FATE

ABB Environmental Inc.,[32] Portland, ME, developed the Fate and Treatability Estimator (FATE) model for the U.S. EPA. This is based on the conceptual model of Namkung and Rittmann for the activated sludge process in a single reactor. It assumes that no volatilization occurs in the primary clarifier and any removal of VOCs is by sorption to solids in the settled solids. It is not widely used by municipal agencies for the estimation of VOC emissions because of the availability of other general fate models that are more comprehensive than the EPA FATE model.

13.7 SOURCE TESTING

Direct measurement of the VOCs emitted from processes that are covered or ducted can be made by sampling and analyzing the exhausted air streams using approved sampling and analytical techniques. Procedures are also available for collecting and analyzing air samples from area sources that are neither ducted nor vented. Approaches for the measurement and monitoring of VOC emission rates are described by the U.S. EPA[33] and Shen, Schmidt and Card[11] for confined and unconfined sources. Isolation flux chambers,[9,10,34] headspace samplers[35] and wind tunnels[36] have been used for measuring VOC emission rates.

Direct measurement methodology is fairly straightforward and the emission estimation rates are accurate and precise as long as the prescribed protocols are followed. Vent gases from liquid stream processes usually contain a lot of moisture and a trap may be required to remove the moisture prior to sampling and analysis.

Several indirect measurement techniques are also available for obtaining VOC emission rates. These include concentration profile technology,[37] transect technology,[34] cross-wind sampling,[38] boundary layer sampling[39] and remote sensing.[33,40] Because indirect methods are affected by meteorological conditions, they may not be advantageous in obtaining a reliable estimate of the VOC emissions. Their utility can be enhanced by using tracer gases released at a known rate. Based on the concentration of the tracer gas in the combined emission, the dilution ratio from which VOC emissions can be empirically modeled can be computed.

13.7.1 CONFINED SOURCES

Confined sources are either ducted or vented. Processes that are amenable for confined point source testing of VOCs include combustion units such as boilers, engines, turbines and incinerators, odor control units such as scrubbers and enclosed biofilters, ducted headwork unit processes, ducted chlorination tanks, exhaust vents of enclosed sludge dewatering facilities, etc. To obtain the mass VOC emission rate, the analytical data are used in conjunction with other parameters measured such as the vent diameter, gas velocity and the concentration of VOCs in the vented gas. An air emission rate (mass of VOCs per unit time) of a source can be computed by multiplying the mass flux rate [(VOC mass/(time × area)] by the surface area of the emission source.

13.7.2 Unconfined Sources

Unconfined sources are area sources such as open grit chambers; aerated and mixed liquid containers such as aeration tanks; nonaerated, nonmixed liquid surfaces such as clarifiers, sludge drying beds, land surfaces, etc. To obtain air samples from unconfined sources, a temporary enclosure and ventilation have to be provided by passing a certain amount of sweep air above the surface of the source. Forced ventilation to collect samples may influence the mass transfer of VOCs between the liquid or solid and gas phases of the unconfined source and hence can affect the VOC emission rates. Air samples are usually collected from aeration tanks and other impoundments by using an isolation flux chamber built to specifications with non-reactive materials.

13.8 TRACER METHOD

This method was originally developed at East Bay Municipal Utility District (EBMUD) in Oakland, California.[41] It uses analogs or surrogates of target VOCs, such as deuterated chloroform ($CDCl_3$) for chloroform, which is not present in the wastewater and is injected into the influent wastewater of a treatment unit. Also, a dye such as rhodamine is injected into the influent stream. The concentrations of these tracers are measured with time in the effluent and gas phases to develop emission factors. The characteristics of tracer compounds should ideally be:

- Representative of the target VOCs
- Easily detectable at low concentrations
- Not normally present in the wastewater
- Not toxic to the treatment process
- Easily handled
- Inexpensive

Tracers such as SF_6 and 4-BFB, rhodamine and $CDCl_3$ are used. Based on the results of an EBMUD study, it was concluded that tracer techniques yield the most accurate estimates of VOC emissions, whereas emission estimates based on a mass balance approach can overpredict VOC emissions. The use of U.S. EPA emission factors can over- or underestimate VOC emissions.[41]

In a Canadian study, SF_6, CO and rhodamine dye were used as tracers to determine the gas and water flow and velocity in sewers, which are needed to predict VOC emissions.[42] In the study, tracer recoveries were within the range of 28 to 74%.

The authors presented data of other investigators[43,44] along with their own data to show that the ratio of predicted to observed gas velocities in the headspace of sewers was in the range of 3 to 10. This overprediction of gas flow velocities would result in an overprediction of VOC emissions.

More full-scale studies are required to fully understand the nuances of the tracer techniques and validate the models developed for assessing VOC losses from collection and wastewater treatment units. Care should be exercised in interpreting the data obtained. Site-specific studies using direct measurements have been shown to be more reliable than predictive modeling tools in the determination of VOC emissions. Modeling techniques, while convenient and less expensive should primarily be used for screening purposes.

13.9 SUMMARY

The determination of VOC emissions from POTW unit processes and collection systems is complex, difficult and costly. However, different methods do exist for estimating VOC emissions from POTWs and industrial sources. These methods are based on approaches such as mass balance, derivation of emission factors, modeling and tracer techniques.

Concentration-based emission factors are superior to flow-based emission factors, because they are related to the measured influent loading of the individual treatment process.[2] Useful examples of derivation of emission factors are provided by the PEEP, JEIP and TriTAC programs conducted in California.

Of all the various models available to municipal agencies, only three have been widely used: WATER7/8/9, BASTE and TOXCHEM/(+). These models have been compared by various investigators[31,45–50] to determine how well the emissions predicted by these models for the same treatment systems would agree. Two detailed case studies on the comparison of basin wide VOC emissions in Chicago and New York using these models are discussed in Chapter 14. The WATER9 model has just been released and emission results based on this model are sparse.

REFERENCES

1. Water Environment Federation/U.S. Environmental Protection Agency Workshop Report and Proceedings: Air Toxics Emissions and POTWs, Arlington, VA, 1990.
2. TriTAC in Collaboration with California POTWs and Air Quality Regulatory Agencies, Guidance Document on Control Technology for Air Emissions from POTWs, March 1994.
3. James M. Montgomery Consulting Engineers Inc., PEEP (Joint Powers Agencies for Pooled Emission Estimation Program) Final Report for Publicly Owned Treatment Works (POTWs), Pasadena, California, 1990.
4. CH2M HILL, JEIP (Joint Emissions Inventory Program) SCAQMD Rule 1179 Emissions Inventory Report, Vol. I, Oakland, California, Volume 1, 1993.
5. U.S. EPA, Compilation of Air Pollution Emission Factors, Vol. I: Stationary Point and Area Sources, Office of Air Quality Planning and Standards, 5th ed., AP-42, 1995.

6. Chang, D.P.Y., Schroeder, E.D. and Corsi, R.L., Emissions of Volatile and Potentially Toxic Organic Compounds From Sewage Treatment Plants and Collection Systems, Report to California Air Resources Board, Contract No. A5-127-32, 1987.
7. Noll, K.E. and De Paul, F.T., Emission of volatile organic compounds from the sewage treatment facilities of the Metropolitan Sanitary District of Greater Chicago, App. P, Water Pollution Control Federation/U.S. EPA Workshop Report and Proceedings: *Air Toxics Emissions and POTWs*, 1990.
8. U.S. EPA, Measurements of Gaseous Emission Rates from Land Surfaces Using an Isolation Flux Chamber — User's Guide, EPA 600/8-86-008 (NTIS PB86-223161), February, 1986.
9. Eklund, B.M., Keinbusch, M.R., Ranum, D. and Harrison, T., Development of a Sampling Method for Measuring VOC Emissions from Surface Impoundments, Radian Corporation, Austin, Texas, 1987.
10. Schmidt, C.E. and Balfour, W.D., Direct gas emission measurement techniques and utilization of emissions data from hazardous waste sites, National Conference of Environmental Engineering Practice, Environmental Engineering Division ASCE, 1983.
11. Shen, T.T., Schmidt, C.E. and Card, T.R. *Assessment and Control of VOC Emissions from Waste Treatment and Disposal Facilities,* Van Nostrand Reinhold, New York, 1993.
12. Pincince, A.B., Transfer of oxygen and emissions of volatile organic compounds at clarifier weirs, *Res. J. Water Pollut. Pollut. Contr. Fed.* 63: 114, 1991.
13. Roberts, P.V., Munz, C. and Dandliker, P., Modeling volatile organic solute removal by surface and bubble aeration, *J. Water Pollut. Contr. Fed.* 56: 157, 1984.
14. U.S. EPA, *User's Guide for WATER9 Software,* Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, February 2001.
15. Olson, D.A., Varma, S. and Corsi, R.L. naUTilus: A Model for Predicting Chemical HAP Emissions form Industrial Sewers, I. User Documentation, II. Technical Documentation, Report to U.S. EPA, 1997.
16. How, C.F.H.H., Maidment, D.R. and Corsi, R.L., Fugitive Emissions of VOCs from Industrial Sewer Networks: Integration of naUTilus and Arcview, Report 98-2, Center For Research in Water Resources, University of Texas, Austin, (www.ce.utexas.edu/centers/crwr/reports/online.html), 1998.
17. Enviromega, Inc., Users' Manual, Toxic Chemical Modeling Program for Water Pollution Control Plants (TOXCHEM+), Version 1, Dundas, Ontario.
18. U.S. EPA, Industrial Wastewater Volatile Organic Compound Emissions — Background Information for BACT/LAER Determinations, EPA/450/3-90-90-004, 1990. U.S. EPA 1994, BACT/LAER Clearing House, www.epa.gov/ttn/catc/products.html#rblcdocs.
19. U.S. EPA, User's Guide for Wastewater Treatment Compound Property Processor and Air Emissions Estimator (WATER8), EPA-453/C-94-080C, November 1994.
20. Corsi, R.L., Chang, D.P.Y. and Schroeder, E.D., A modeling approach for VOC emissions from sewers, *Water Environ. Res.,* 64: 734, 1992.
21. Nakasone, H., Study of aeration at weirs and cascades, *J. Environ. Eng.,* ASCE, 113: 64, 1986.
22. Corsi, R.L. and Quigley, C., Design of low emission sewers, Proc. 87th Annual Meeting and Exposition of the Air and Waste Management Association, Cincinnati, Ohio, Paper No. 94-WP92.01, 1994.

23. Corsi, R.L., Birkett, S., Melcer, H. and Bell, J., Control of VOC emissions from sewers: A multiparameter assessment, *Water Sci. Technol.,* 31: 147, 1995.
24. Parkhurst, J.D. and Pomeroy, R.D., Oxygen absorption in streams, *J. Sanitary Eng. Div. SA1*, ASCE, 101, 1972.
25. Mackay, D. and Yeun, A., Mass transfer coefficient correlations for volatilization of organic solutes from water, *Environ. Sci. Technol.,* 17: 211, 1983.
26. Baillod, C.R., Crittenden, J.C., Mihelcic, J.R., Rogers, T.N. and Grady, C.P.L., Critical Evaluation of the State of Technologies for Predicting the Transport and Fate of Toxic Compounds in Wastewater Facilities, Report of WPCF Research Foundation Project 90-1, 1990
27. CH2M HILL, User's Manual, Bay Area Sewage Toxics Emission Model (BASTE), Version 3, Oakland, California, 1992.
28. Govind, R., Lai, L. and Dobbs, R., Integrated model for predicting the fate of organics in wastewater treatment plants, *Environ. Prog*., 10: 13, 1991.
29. Barton, D.A., NCASI Organic Compound Elimination Pathway Model, Version 1.34, National Council for Air and Stream Improvement, 1988.
30. Clark, B., Mackay, D., Tsafi, L., Henry, G.L.H. and Salenieks, S., *A Model of Organic Chemical Fate in a Biological Wastewater Treatment Plant,* Institute of Environmental Studies, University of Toronto, Ontario, 1990.
31. Schroy, J.M., Evaluation of emissions from wastewater treatment systems — a comparison of available software performance, paper presented at the AIChE Annual Summer National Meeting, 1994.
32. ABB Environmental, Inc., Fate and Treatability Estimator, Technical Documentation and Users' Manual, June 1990.
33. U.S. EPA, Air Superfund National Technical Guidance Study Series, Vol. 2: Estimation of Baseline Air Emissions at Superfund Sites, Interim Final, Office of Air Quality Planning and Standards, EPA 450/1-89/004, 1989.
34. Balfour, W.D., Schmidt, C.E. and Eklund, B.M., Sampling approaches for measuring emission rates from hazardous waste disposal facilities, Paper 84-3.3 presented at the Annual Air and Waste Management Association Meeting, 1984.
35. Kapling, E.J., Kurtz, A.J. and Rahimi, M., VOC sampling for emission rate determination and ambient air quality on an inactive landfill, paper presented at the New England Section of the Air Pollution Control Association, Fall Conference, Worcester, Massachusetts, 1986.
36. Cowherd, C., Measurement of particulate emissions from hazardous waste disposal sites, paper presented at the 78th Annual Meeting of the Air Pollution Control Association, Detroit, 1985.
37. Thibodeaux, L.G., Parker, D.G. and Heck, M.M., Measurements of Volatile Chemical Emissions from Wastewater Basins, EPA 600/5-2-82/095, 1982.
38. Wisner, C.E. and Davis, T.W., Characterization of fugitive emission rates using a mobile integrating sampler, Proc. 1989 EPA/AWMA Symposium on Measurement of Toxic and Related Air Pollutants, Raleigh, North Carolina, 1989.
39. Esplin, G.J., Boundary layer emissions monitoring, *J. Air Pollut. Contr. Assoc.,* 38: 1158, 1988.
40. McLaren, S.E. and Stedman, D.H., Flux measurements using simultaneous long path ultraviolet and infrared spectroscopy, Proc. 83rd Annual Meeting of the Air and Waste Management Association, Pittsburgh, 1990.

41. Hellier, W.G., EBMUD monitoring program for air toxics emissions, paper presented at the Joint EPA/WPCF Workshop on Air Toxics Emissions and POTWs, July 9–11, Alexandria, Virginia, 1989.
42. Bell, J.P., Monteith, H., Parker, W.J., Melcer, H., Corsi, R.L. and Zytner, R., Modeling the Stripping and Volatilization of VOC in Wastewater Collection and Treatment Systems, Report of Water Environment Research Foundation Project 91-TFT-1, Alexandria, VA, 1998.
43. Pescod, M.B. and Price, A.C., Major factors in sewer ventilation, *J. Water Poll Contr. Fed.,* 54: 385, 1982.
44. Quigley, C.J. and Corsi, R.L., Emissions of VOCs from a Municipal Sewer, *J. Air Waste Mgmnt.. Assoc.,* 45: 395, 1995.
45. Tata, P., Soszynski, S., Zenz, D.R., Lordi, D.T. and Lue-Hing, C., Volatile organic compound emissions from the water reclamation plants of the Metropolitan Water Reclamation District of Greater Chicago, paper presented at the Water Environment Federation Specialty Conference on Control of Emissions of Odors and Volatile Organic Compounds, Jacksonville, Florida, 1994.
46. Tata, P., Soszynski, S., Lordi, D.T., Zenz, D.R., Lue-Hing, C. and Card, T., Prediction of volatile organic compound emissions from publicly owned treatment works, Proc. 68th Annual Water Environment Federation Conference, Miami Beach, Florida, 1995.
47. Tata, P., Lordi, D.T., Soszynski, S., Zenz, D.R. and Lue-Hing, C., Emission of Volatile Organic Compounds from Water Reclamation Plants of Metropolitan Water Reclamation District of Greater Chicago, Report No. 98-30, Research and Development Department, Chicago, 1998.
48. Ferro A.R. and Pincince, A.B., Comparison of computer programs for estimating emissions of volatile organic compounds from wastewater treatment facilities, paper presented at the Annual Conference and Exposition of the Water Environment Federation, 1992.
49. Mayer, G.J., Cheng, I.S., Pau, P. and Mohamed, F., Emissions of air toxics from wastewater treatment plants, *Water Env. Res.,* 66: 140, 1994.
50. New York City Department of Environmental Protection, Malcolm Pirnie Inc. and Illinois Institute of Technology, Analysis of Volatile Organic Compound Emissions from the New York City Wastewater Collection/Treatment System, 1990.

14 VOC Emissions from Wastewater Treatment Facilities

Prakasam Tata, Jay Witherspoon and Cecil Lue-Hing

CONTENTS

14.1 Introduction 284
14.2 Quantitation of VOCS by Emission Factors 284
  14.2.1 PEEP Emission Factors 285
  14.2.2 JEIP Emission Factors 285
  14.2.3 TriTAC Emission Factors 290
14.3 VOC Emissions from POTWs by General Fate Models 290
14.4 Comparative Evaluation of the Performance of Noncomprehensive Fate Models 297
14.5 Comparative Evaluation of the Performance of Comprehensive Fate Models 297
  14.5.1 The Metropolitan Water Reclamation District of Greater Chicago Studies 299
    14.5.1.1 VOC Emission Estimates Computed by WATER7 Model Using the Compound Parameters of the WATER7, BASTE and TOXCHEM Models 299
    14.5.1.2 VOC Emission Estimates Computed by the BASTE Model Using the Compound Parameters of the WATER7, BASTE and TOXCHEM Models 306
    14.5.1.3 VOC Emission Estimates Computed by the TOXCHEM Model Using the Compound Parameters of the WATER7, BASTE and TOXCHEM Models 306
    14.5.1.4 Comparison of Directly Measured VOC Emission Rates and Model-Predicted VOC Emission Rates 307

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

14.5.2 The New York City Department of Environmental Protection Studies 308
14.6 Summary 312
References 313

14.1 INTRODUCTION

As indicated in Chapter 13, VOC emission rates can be derived by using emission factors, general fate models and direct source testing. This chapter discusses the quantitation of VOC emissions from the unit processes of wastewater treatment facilities by using emission factors, results of VOC emissions reported by a few major municipal agencies based on general fate model methodology and how these emission estimates compare with directly measured emission rates.

14.2 QUANTITATION OF VOCs BY EMISSION FACTORS

By far the simplest and most inexpensive method of estimating VOC emissions from wastewater treatment facilities is based on the use of emission factors. Emission factors for unit processes of POTWs were derived in the previously conducted PEEP[1], JEIP[2] and TriTAC[3] studies.

To obtain the emission rate of a VOC from a given unit process of a POTW, the emission factor of the VOC for the unit process specified in the PEEP program is multiplied by the influent mass loading rate of the same VOC to that unit. The sum total of the annual emission rates of all VOCs from the unit processes of a POTW gives the total VOC emission rate of the POTW. A major objective of the PEEP study was to provide 25 public agencies in California with a standardized estimation method for air emissions from liquid-, solid- and gas-handling processes. The emission factors developed in this study were based on actual field measurements.

Emission factors were developed in the JEIP study for 43 unit processes at 22 California POTWs. Mean, median and range-of-emission factors for the unit processes were summarized. Using these factors, the sum total of the emission rate of all VOCs for a specific unit process of any POTW can be estimated by multiplying the relevant JEIP emission factor with the mass VOC loading to the same type of unit of the POTW. The emission rate of VOCs at a POTW can be obtained by summing up the individual unit process VOC emission rates. A major objective of the JEIP study was to gain knowledge on the VOC emissions from POTWs relative to other source categories in the South Coast Air Basin of California. Emission factors were also developed based on actual field measurements.

In the TriTAC study, emission factors were reported for various unit processes for both total VOCs as well as individual species based on concentration of the influent VOCs as well as sewage flow treated. In addition to the flow- and concentration-based emission factors, emission rates based on fate modeling were used in the study. The overall study objective was to provide guidance on identifying appropriate technologies for controlling VOC emissions from POTWs.

14.2.1 PEEP EMISSION FACTORS

A summary of the median emission factors developed for different VOCs for the various PEEP unit processes is presented in Table 14.1. These emission factors were derived based on the procedures described in the previous chapter. It should be recognized that the emission factors are derived for POTWs examined under the PEEP program and may not be able to be directly applied to unit processes of POTWs located elsewhere. However, they offer an approximation of VOC emission rates for screening purposes. In sizing VOC control technology units and in dealing with regulatory compliance issues, it is prudent to use emission factors developed under site-specific conditions and approved by regulatory agencies.

In Table 14.2, the PEEP emission factors for the air-activated sludge process are compared with those derived in a Canadian study.[4] A comparison of the PEEP emission factors and those derived for aerated grit chambers in the same study is presented in Table 14.3.

The PEEP study investigators concluded that the PEEP and Canadian study emission factors are comparable.[2] They justified their conclusion based on their observing reasonably comparable values of saturation fractions of VOCs with the aeration devices' detention times in the grit and aeration chambers and the ratio of air to liquid used. However, a close examination of the data presented does not justify this conclusion. This underscores the limitations of using emission factors previously derived at a specific location to estimate the emission rates at a different location.

Emission factors and emission rates of POTWs can vary significantly depending on whether a POTW treats wastewater exclusively from residential areas, domestic sources (i.e., residential, some industrial and commercial sources) or industrialized areas. Emissions (expressed as μg/L of wastewater treated) from a residential POTW, a domestic POTW and an industrialized POTW were previously reported by Caballero[5] and are compared in Table 14.4.

14.2.2 JEIP EMISSION FACTORS

Table 14.5 summarizes the averages of JEIP emission factors and their ranges for total VOCs for various unit processes.[2] These factors are derived based on the summation of all the directly measured emission masses and the total VOC mass loadings to the various units. JEIP emission factors are also available for individually speciated VOCs for each of the unit processes of all participating agencies in the JEIP program, as in the case of the PEEP study. It is beyond the scope of this chapter to include all these emission factors, but the range of these emission factors for various combustion devices is presented in Table 14.6. The total VOC mass emission rate is computed by multiplying the emission factors with millions of cubic feet of digester gas used in the combustion device.

As can be seen from Table 14.6, each combustion source has a wide range for the emission factors. This is probably due to the differences in operating conditions and the efficiency of performance of the combustion devices. If accurate VOC mass emissions are required for potential permit compliance, designing control technology

TABLE 14.1
Pooled Emission Estimation Program (PEEP) Factor for POTW Unit Operations

Compounds	Median Emission Factors							
	Aerated Grit Chamber	Primary Settling Tank	Air Activated Sludge	Mechanically Mixed Air Activated Sludge	Pure O_2 Activated Sludge	Trickling Filter	Secondary Clarifier	Tertiary Filter. Quiescent Zone
Benzene	3.2E – 02			0.0E + 00	0.0E + 00			
Carbon tetrachloride								
Chloroform	3.7E – 03	0.0E + 00	2.6E – 1	2.2E – 01	5.0E – 04	5.6E – 01	2.1E – 03	5.5E – 04
Dichlorobenzene	0.0	0.0E + 00	1.2E – 01		0.0E + 00	0.0E + 00	0.0E + 00	0.0E + 00
1,4-Dioxane			4.8E – 05					
Ethylene dibromide								
Ethylene dichloride			0.0E + 00					
Methylene chloride	2.1E – 03	3.1E – 03	1.3E – 01		5.6E – 04			
Tetrachloroethylene	6.8E – 03	0.0 + 0	3.3E – 01		3.5E – 03		8.0E – 04	
Styrene								
1,1,1-Trichloroethane	1.1E – 02	0.0E + 00	4.6E – 01		1.5E – 03	1.1E + 00	8.5E – 04	8.5E – 04
Trichloroethylene	1.E – 02	3.4E – 02	3.3E – 01		0.0E + 00			
Trichlorofluoromethane	0.E + 00							
Toluene	1.3E – 03	3.9E – 03	1.6E – 01		–3.0E – 06	3.5E – 01		
Vinyl chloride								
Vinylidene chloride		0.0E + 00						
Xylenes	2.5E –04		1.1E – 01		3.9E – 07	2.5E – 01		
Formaldehyde	–6.4E – 06	6.3E – 05	2.1E – 04		4.8E–08			8.3E – 07

	Median Emission Factors							
Compounds	**Dechlorination Chamber**	**Dechlorine Contact Tank**	**DAF Thickener**	**Gravity Thickener**	**Anaerobic Digester**	**Belt Filter Press**	**Sludge Centrifuge**	**Sludge Drying Beds**
Benzene	7.5E−01				2.0E + 00	2.7E−01	1.1E−02	
Carbon tetrachloride	1.0E + 00							
Chloroform	1.1E−01	2.8E−03	2.0E−01	5.3E−02	0.0E + 00			
Dichlorobenzene	3.1E−01			0.0E + 00	3.9E−01	0.0E + 00	1.0E−02	0.0E + 00
1,4-Dioxane								
Ethylene dibromide								
Ethylene dichloride	3.5E−01							
Methylene chloride			2.0E−01	1.0E−01	0.0E + 00			
Tetrachloroethylene	1.7E−01		2.9E−01	5.3E−02	1.9E−01			
Styrene	6.4E−01				0.0E + 00			
1,1,1-Trichloroethane	4.9E−01	5.3E−03	6.8E−01	1.0E−01	2.2E−01			
Trichloroethylene	7.6E−01			5.4E−02				
Trichlorofluoromethane								
Toluene	6.9E−01			5.1E−02	2.1E + 00	4.5E−01	2.1E−01	5.2E + 00
Vinyl chloride								
Vinylidene chloride								
Xylenes	7.3E−01				1.2E + 00	9.8E−02	2.3E−02	4.5E + 00
Formaldehyde	4.3E−01	5.1E−06	1.3E−04	−7.7E−05	1.5E−04	9.2E−03	2.7E−04	7.6E−02

TABLE 14.2
Comparison of PEEP and Environment Canada Emission Factors for Diffused Air Activated Sludge

Compound	PEEP Emission Factors (Median)	Environment Canada Emission Factors Average of 2 Sites	Average of 4 Sites
Ethylene dichloride	0.00	0.07	0.23
Dichlorobenzene	0.12	0.17	0.22
Methylene chloride	0.13	0.17	0.69
Chloroform	0.26	0.15	0.31
1,1,1-Trichloroethane	0.46	0.66	0.61
Xylenes	0.11	0.15	0.31
Benzene			0.23
Toluene	0.16	0.34	0.69
Trichloroethylene	0.33	0.01	0.20
Tetrchloroethylene	0.33	0.74	0.59
1,4-Dioxane	0.0		

Source: James M. Montgomery Consulting Engineers Inc., Joint Powers Agencies for Pooled Emission Estimation Program (PEEP), Final Report for Publicly Owned Treatment Works (POTWs), Pasadena, California, 1990.

TABLE 14.3
Comparison of PEEP and Canadian Study Emission Factors — Aerated Grit Chamber

Compound	PEEP (Median)	Environment Canada 3 Sites (Median)	3 Sites (Average)
Ethylene dichloride		0.0006	0.0006
Dichlorobenzene	0.0000	0.0013	0.0018
Methylene chloride	0.0021	0.0100	0.0078
Chloroform	0.0037	0.0036	0.0029
1,1,1-Trichloroethane	0.0109	0.0038	0.0047
Xylenes	0.0003	0.0024	0.0057
Benzene	0.0319	0.0117	0.0117
Toluene	0.0013	0.0035	0.0070
Trichloroethylene	0.0104	0.0003	0.0021
Air:Water Ratio	0.15	0.08	0.12

TABLE 14.4
Comparison of Emissions from Different Types of POTWs

Type of POTW	VOC Emissions (μg/L of Waste Treated)
Residential	3
Domestic	30
Industrial	40

Source: Caballero, R., VOC emissions from POTWs, Appendix I, paper presented at the Joint U.S. EPA/WPCF Workshop on Air toxics Emissions and POTWs, Alexandria, Virginia, 1989.

TABLE 14.5
Averages and Ranges of Emission Factors Derived for Various Unit Processes in the JEIP Study

Unit Process	Average	Range
Primary sedimentation tank	0.063	0.019-0.083
Flow equalization tanks		
Primary effluent	0.451	Not applicable
Secondary effluent	1.391	Not applicable
Diffused air activated sludge	0.281	0.081 — 0.799
Mechanical activated sludge	0.065	Not applicable
Trickling filters	0.279	0.078 — 0.481
Secondary clarifiers	0.096	0.027 — 0.226
Gravity filtration	0.013	0.004 — 0.03
Chlorination	0.019	0.01 — 0.027
Final effluent weir	0.001	0.00008 — 0.0014
Dissolved air flotation	0.94	0.075 — 1.815
Sludge dewatering centrifuges	3.7×10^{-6} lb VOC/gal	Not applicable
Belt press sludge dewatering	160×10^{-7} lb VOC/gal	$2 — 322 \times 10^{-7}$ lb VOC/gal
Sludge conveyor	$1.7 \times \times 10^{-9}$ lb VOC/lb solids	$1.3 — 2 \times 10^{-9}$ lb VOC/lb solids
Sludge cake -storage	$2.3 \times \times 10^{-9}$ lb VOC/lb solids	$2.2 — 2.4 \times 10^{-9}$ lb VOC/lb solids
Sludge truck loading	1.4 × 10-9 lb VOC/lb solids	Not applicable

Source: JEIP[2]

TABLE 14.6
JEIP Combustion Source Emission Factors

Source and Fuel	Range lb VOC/(mmcf*)	Selected Default lb VOC/(mmcf)
IC Engine — Digester Gas	0.41 — 168	0.27
IC Engine — Natural Gas	7 — 280	280
Boiler — Digester Gas	1.6 — 4	4
Boiler — Natural Gas	7	7
Flare — Digester Gas	0.41 — 27.8	4.3
Turbine — Digester Gas	2.6 — 3.4	3.0

* mmcf = million cubic feet of gas

Source: JEIP[2]

devices and emissions trading, it is prudent to do site-specific direct source testing to obtain reliable estimates of the quantity and rate of such emissions.

14.2.3 TriTAC Emission Factors

Table 14.7 lists the emission factors reported in the TriTAC study.[3] They are based on both the influent flow and concentration of the total and individual VOCs in the influent to the unit process. The total VOCs are determined by U.S. EPA Method 25.2 and the individual VOCs by other U.S. EPA methods.

In view of the observed differences among the emission factors obtained in different studies conducted at specific locations, one must be careful in using them for different locations. The emission factors can be used for screening purposes and should be carefully evaluated for sizing VOC control equipment. It is prudent to consult with state regulatory agencies and seek their approval before using emission factors in making critical decisions with regard to compliance issues, emissions trading or the design and installation of VOC control equipment at a POTW.

14.3 VOC EMISSIONS FROM POTWS BY GENERAL FATE MODELS

General fate models are convenient tools for determining the fate and predicting the emission rates of VOCs from POTWs without undertaking elaborate and expensive sampling and analysis of directly emitted emissions of VOCs from the various POTW unit processes. When adequately calibrated models are used with proper input parameters, the models simulate material balances around a particular unit process or a combination of unit processes composing the POTW. However, the accuracy and reliability of the predicted estimates, in comparison with the directly measured emissions, greatly depend on validating the calibrated model and the robustness of the input parameters. The reliability of the directly measured VOC emissions also depends on various factors. These include: (1) frequency of measurements; the

TABLE 14.7
TriTAC Emission Factors of Various VOCs for Computing and Screening of Emissions from Different POTW Unit Processes

Unit Process	Compounds and Range of Concentration	Emission Factors Flow based (lb/yr/mgd)	Emission Factors Conc. based (lb/lbs infl.)	Comments (Direct Measurement Most Appropriate)
Headworks	Total VOCs (1–10 PPMV)	0.1	NA	
Grit Removal	Total VOCs (1–10 PPMV)	7.0	NA	Emission factors are for aerated grit chambers. For nonaerated grit chambers, strata available in original data sources.
	Benzene	0.30	0.30	
	Ethyl benzene	0.21	0.03	
	Toluene	5.9E-02	1.3E-03	
	Xylene	1.6E-02	2.5E-04	
	1,1,1-Trichloroethane	1.5E-01	1.5E-02	
	Chloroform	6.6E-02	3.7E-03	
	Methylene chloride	7.0E-02	2.1E-03	
	Tetrachloroethylene	1.8E-01	6.8E-03	
	Acetone	8.1E-01	2.5E-04	
	MEK	0.16	4.3E-03	
	MIBK	1.5E-01	4.31E-04	
Primary Sedimentation	Total VOCs (10–100 PPMV)	40	0.06	
	Benzene	4.1E-02	4.3E-03	
	Ethyl benzene	2.9E-02	3.7E-03	
	Toluene	0.18	3.9E-03	
	Xylene	1.6E-02	2.5E-04	
	1,1,1-Trichloroethane	4.0E-02	2.9E-03	
	Chloroform	5.6E-02	3.1E-03	
	Methylene chloride	0.10	3.1E-03	
	Tetrachloroethylene	7.1E-02	2.8E-03	
	Acetone	5.1	1.6E-03	
	MEK	1.02	2.7E-02	
	MIBK	0.93	2.7E-03	
Flow Equalization	Total VOCs (0–2 PPMV)	30	1.4	Emission factors are for secondary effluent equalizations. No other individual VOC data are available. JEIP data available for primary storage.

TABLE 14.7 (CONTINUED)
TriTAC Emission Factors of Various VOCs for Computing and Screening of Emissions from Different POTW Unit Processes

Unit Process	Compounds and Range of Concentration	Emission Factors		Comments (Direct Measurement Most Appropriate)
		Flow based (lb/yr/mgd)	Conc. based (lb/lbs infl.)	
	Acetone	4.7	1.4E-03	
	MEK	0.94	2.5E-2	
	MIBK	0.85	2.5E-03	
Diffused Air Activated Sludge	Total VOCs (1–10 PPMV)	190	0.13	
	Benzene	1.7	0.18	
	Ethyl benzene	1.2	0.15	
	Toluene	7.3	0.16	
	Xylene	7.0	0.11	
	1,1,1-tri-chloroethane	6.5	0.46	
	Chloroform	4.7	0.26	
	Methylene chloride	4.3	0.13	
	Tetrachloroethylene	8.5	0.33	
	Acetone	3.2E-02	9.9E-06	
	MEK	6.4E-3	1.7E-4	
	MIBK	5.8E-03	1.7E-05	
Mechanical Aeration	Total VOCs (1–10 PPMV)	30	0.06	Emission factors affected by number of aerators and hp
	1,1,1-Trichloroethane	2.9	0.2	
	Chloroform	3.9	0.22	
	Methylene chloride	7.3	0.22	
	Tetrachloroethylene	5.0	0.20	
	Acetone	4.7	1.4E-03	
	MEK	0.94	2.5E-2	
	MIBK	0.85	2.5E-03	
Secondary Clarifier	Total VOCs (0–2 PPMV)	12	0.1	
	Benzene	NA	NA	
	Ethyl benzene	NA	NA	
	Toluene	NA	NA	
	Xylene	NA	NA	
	1,1,1-Trichloroethane	1.2E-02	8.5E-04	
	Chloroform	3.8E-02	2.1E-03	
	Methylene chloride	7.0E-02	2.1E-03	
	Tetrachloroethylene	2.1E-02	8.0E-04	
	Acetone	12.1	3.7E-03	

TABLE 14.7 (CONTINUED)
TriTAC Emission Factors of Various VOCs for Computing and Screening of Emissions from Different POTW Unit Processes

Unit Process	Compounds and Range of Concentration	Emission Factors: Flow based (lb/yr/mgd)	Emission Factors: Conc. based (lb/lbs infl.)	Comments (Direct Measurement Most Appropriate)
	MEK	2.4	6.5E-2	
	MIBK	2.19	1.5E-03	
Effluent Filtration	Total VOCs (0–2 PPMV)	0.6	0.01	
	Benzene	8.9E-03	9.4E-04	
	Ethyl benzene	6.2E-03	8.0E-04	
	Toluene	3.9E-02	8.5E-04	
	Xylene	5.5E-02	8.7E-04	
	1,1,1-Trichloroethane	7.2E-03	5.1E-04	
	Chloroform	9.9E-03	5.5E-04	
	Methylene chloride	1.8E-02	5.5E-04	
	Tetrachloroethylene	1.3E-02	4.9E-04	
	Acetone	NA	NA	
	MEK	NA	NA	
	MIBK	NA	NA	

greater the number of measurements the better the reliability, (2) methods and reliability of sampling, compositing and analytical techniques used and (3) spatial and temporal effects.

Several general fate models have been developed and reported in the literature. In the late 1970s and early 1980s, various noncomprehensive fate models were developed to predict VOC emissions from mostly activated sludge basins.[6–10] These first-generation models were usually programmed as spreadsheets — typically with a fixed configuration — and basically dealt with activated sludge or other single unit aeration processes. Software was provided only to input data in a prescribed format and usually did not have the facility to reflect the true flow chart of an actual POTW. The noncomprehensive models did not have the ability to simulate fixed film processes such as trickling filters and rotating biological contactors.

However, the next-generation models — particularly WATER7/8/9, BASTE and TOXCHEM/(+) — are by far the most comprehensive models and are accepted by the profession as well as several state regulatory agencies. These models have the ability to model many of the common unit processes present at POTWs. In view of the complex and expensive nature of direct-measurement methodology to determine VOC emissions, these models are extensively used and studied by various large POTWs for estimating VOC emissions. Many POTWs have used these models to ascertain whether the POTWs are “major” sources of VOC emissions and need to be subjected to the Title V permit process if and when a MACT standard is promulgated.

Also, these models can be used to determine whether retrofitting or modifying the existing POTWs with alternative unit processes would yield lower emissions. For example, Monteith et al.[11] used the TOXCHEM model to conclude that the emissions of toluene and tetrachloroethylene could be reduced by replacing the existing coarse bubble aeration system of a POTW in Minnesota with a fine bubble aeration system. General fate models also can be used for evaluating whether an industrial waste can be treated in a municipal wastewater treatment plant without creating a problem due to excess VOC emissions.[12] They are also used to determine the trend of VOC emissions from POTWs over a number of years.[13]

In response to the 1990 CAAA, major wastewater agencies made a significant effort to make an estimate of their annual VOC emission rates to determine whether they would be characterized as "major" sources. Also, emission rate estimates were used to determine whether there was a potential health risk to the surrounding community of POTWs.[14,15] Hentz et al.[16] reported air emissions from the Philadelphia's Northeast (flow: 188 mgd), Southeast (flow: 104 mgd) and Southwest (flow: 178 mgd) water pollution control plants (WPCPs). The annual VOC emission rates were derived using the TOXCHEM model. In their studies, the authors first validated the model by extensively comparing and iterating the model-predicted target HAPs emissions with the directly measured HAPs emissions from various unit processes. The air samples from the unit processes were collected by using flux chamber Summa canisters and were analyzed by U.S. EPA Method TO-14.

The results reported from these studies are presented in Table 14.8, Table 14.9 and Table 14.10. Table 14.8 presents the HAPs concentrations in the influents of these WPCPs and the emissions predicted by the validated model. The HAPs reported in the table represent in general more than 99 and 97% of the HAP mass detected in the influent and air samples, respectively. Table 14.9 presents the modeled emissions of total HAPs and other tentatively identified compounds (TICs) along with directly measured emissions from various unit processes of the WPCPs. An extensive effort was made to calibrate the TOXCHEM model over several years in carefully managed pilot plant studies. Although the model was calibrated using directly measured values, the emissions were still somewhat higher than the model-derived emissions. This was attributed to methanol emissions, which could be measured directly, whereas methanol could not be detected in the influent by the analytical method used. The influent methanol concentration is zero and hence, model-predicted emissions were also zero. The total VOC emissions presented in Table 14.10 also include emissions from combustion sources such as digester gas flares, incinerators, TICs and other emissions from miscellaneous sources such as fuel tanks and small sludge storage tanks.

From the literature it is not clear whether models calibrated with a set of directly measured VOC emissions or effluent VOC concentrations would yield emission estimates that would be comparable to emission rates based on direct measurements of VOCs made at another time.

Mayer et al.[17] reported on the emissions from the Hyperion, Terminal Island, Tillman and LA-Glendale treatment plants operated by the City of Los Angeles The emission rates reported for various VOCs are given in Table 14.11. The authors also made a comparison of chloroform emissions derived by a mass balance approach,

TABLE 14.8
HAP Measurements (kg/yr)

	Northeast WPCP		Southeast WPCP		Southwest WPCP	
Compound	**Influent**	**Emissions**	**Influent**	**Emissions**	**Influent**	**Emissions**
Acetone	72,560	54	22,675	0	68,025	98
Benzene	1,451	209	0	2	2,177	122
Chloroform	1,995	726	1,270	132	1,451	68
1,4-Dichlorobenzene	363	159	218	26	254	22
1,2-Dichloroethane	2,268	222	0	0	0	4
Ethylbenzene	272	63	63	3	816	50
Isopropylbenzene	11,338	862	0	2	0	25
Methanol	0	907	0	29	0	544
Methylene chloride	1,088	231	263	23	1,224	43
Methyl ethyl ketone	1,814	5	245	0	10,884	3
Naphthalene	1,088	0	172	0	1,406	0
Styrene	6,803	213	0	0	9	4
Tetrachlorethylene	1,995	1,678	635	181	1,179	240
1,2,4-Trichlorobenzene	0	2	281	73	0	0
1,1,1-Trichloroethane	363	258	63	25	254	45
Trichoroethene	363	336	145	29	327	27
Toluene	2,902	363	381	18	5,442	544
Xylenes	1,542	240	363	18	3,900	254
Sum targets	108,205	6,529	26,775	562	97,348	2,064
Percent emitted		16		13		5

Source: Hentz et al. personal communication, 2000.

PEEP emission factor, BASTE model and direct measurement. These values for the Hyperion plant were 2.39, 0.54, 0.74 and 1.60 tons/year, respectively. For the Tillman plant, the comparable values were 80.09, NA (not available), 0.09 and 0.11 tons/year, respectively. Since chloroform is a relatively nonbiodegradable compound, the emissions derived by a mass balance approach and direct measurement were reasonable in the case of Hyperion plant. However, in the case of the Tillman plant, a considerably higher emission of chloroform was observed by direct measurement than by a mass balance approach. These differences are probably due to the spatial and temporal differences in sampling frequency, the number of observations and measurements used in the computation of emission rates and, perhaps, differences in the method detection limits of liquid and air analyses.

Comparative studies using the same influent VOC concentration datasets have shown considerable variation in the outputs or emissions estimated by various noncomprehensive as well as comprehensive general fate models. In a study conducted at the Metropolitan Water Reclamation District of Greater Chicago, Tata et al.[18] compared the total emissions of various VOCs for the years 1987 through 1992 from aeration basins of the Stickney, North Side and Calumet Water Reclamation Plants using the noncomprehensive models of Namkung and Rittmann[6], Barton[8] and

TABLE 14.9
Total HAP Emissions (kg/yr)

	Northeast		Southeast		Southwest	
Source	Emissions	Model	Emissions	Model	Emissions	Model
Measured air sources						
Flocculation tanks			140	110	1,600	540
Primary clarifiers	2,300	2,400	9a	310	360 a	950
Activated sludge processes	4,400	3,800	390	110	20	5
Mixed liquor channels			50	20	160	29
DAFTs	5	100			5	82
Subtotal (kg/yr)	6,700	6,300	590	550	2,150	1,600
Modeled air sources						
Influent pumps and channels		3		4		77
Grit basins		10				10
Mixed liquor channels		77				
Secondary clarifiers		150		14		100
Chlorination and effluent		10		1		5
Digester flares		5				8
Subtotal (kg/yr)		260		20		200
Total HAPs (kg/yr)	6,700	6,600	590	570	2,150	1,800
Total HAPs (kg C/yr)	2,500	3,300	200	270	1,300	1,300
Total TICs (kg C/yr)	7,400	9,100	200	200	1,300	1,600
Total VOCs (kg C/yr)	9,900	12,400	400	470	2,600	2,900

[a] Emissions only from primary weirs.

Source: Hentz et al. personal communication, 2000.

U.S. EPA's TSDF models.[9] Also, the more comprehensive models of FATE, CINCI, WATER7 and BASTE were compared with each other for their annual VOC emission rate outputs. Wide variations in the predicted estimates yielded by noncomprehensive models were observed. The comprehensive fate models also showed wide variations in the predicted VOC emission rates; WATER7 consistently predicted higher VOC emissions than the others. Similar overpredictions by the WATER7 model for different VOCs were also reported by others,[15,19]

The Metropolitan Water Reclamation District of Greater Chicago (MWRDGC) conducted detailed studies to determine the annual VOC emission rates from its seven water reclamation plants.[20] In this study, the VOC emission rates computed by the general fate models were also compared. Malcolm Pirnie, Inc. and the Illinois Institute of Technology, Chicago jointly conducted similar studies to compare the annual emission rates of the 14 water pollution control plants owned and operated by the Department of Environmental Protection, New York.[15] TOXCHEM, WATER7 or WATER8 and BASTE models were used to compute the annual emission rates in these studies. In both the Chicago and New York studies, direct measurements of VOCs were also made to compare the measured emission rates with the model-predicted emission rates. In addition, outputs of each of these models derived by

TABLE 14.10
Total VOC Emissions (kg/yr)

Emission Source				
No.	**Description**	**Annual Northeast VOC Emissions (@ 188 MGD)**	**Annual Southeast VOC Emissions (@ 104 MGD)**	**Actual Southwest VOC Emissions (@ 178 MGD)**
1	Influent pumps & channels	2	1	68
2	Grit basins	8	2	14
3	Flocculation tanks		130	730
4	Primary sedimentation tanks	3,000	150	640
5	Rbc/activated sludge process	9,100	150	
6	Pure oxygen aeration tanks			450
7	Mixed liquor channels	36	13	77
8	Secondary sedimentation tanks	95	5	360
9	Chlorination & effluent channels	6	1	18
10	Dissolved air flotation tanks	100		440
11	Anaerobic digester flares	12		60
12	Incinerators	77		440
13	Miscellaneous sources	1,900	18	1,300
Total Annual VOC Emissions Estimates				
	Actual (kg VOC as carbon per year)	14,336	470	4,597

using the default coefficients embedded in the models were compared with those derived by substituting the fate mechanisms coefficients of the other models.

14.4 COMPARATIVE EVALUATION OF THE PERFORMANCE OF NONCOMPREHENSIVE FATE MODELS

Tata et al.[20] examined the estimated VOC emissions from various water reclamation plants operated by the MWRDGC and reported variations in the estimates predicted by noncomprehensive models of Namkung and Rittmann, Barton and U.S. EPA's TSDF. As an example, the annual VOC emission rates predicted by these models from the aeration basins of the Stickney Water Reclamation Plant, which had a flow range of 27 to 42 m^3/s (616 to 959 mgd) during 1987 through 1992 are shown in Table 14.12. These emission rates could not be compared with actual emission rates because direct measurements of these emissions were not made.

14.5 COMPARATIVE EVALUATION OF THE PERFORMANCE OF COMPREHENSIVE FATE MODELS

Detailed studies were conducted by Tata et al.[20] to compare the annual VOC emission rates from the seven water reclamation plants owned and operated by the MWRDGC.

TABLE 14.11
Summary of VOC Emissions of City of Los Angeles POTWs (kg/yr)

	Hyperion	Terminal Island	Tillman	LA-Glendale
Compounds				
Methylene chloride	4,337	249	600	444
Chloroform	2,678	140	82	116
Benzene	163	108	3	1
Tetrachloroethene	6,163	222	1,991	662
Carbon tetrachloride	12	2	0	0
Toluene	3,429	322	46	27
Total xylenes	3,683	215	294	72
1,1,1-Trichloroethane	9,558	163	1,729	297
Dichlorobenzene	336	0	55	3
1,2-Dichloroethane	6	4	0	0
Trichloroethene	366	12	3	5
1,1-Dichloroethene	4	3	0	0
Vinyl chloride	14	3	0	0
Formaldehyde	391	NA	NA	NA
Acetaldehyde	63	NA	NA	NA
Total dioxins	2.0E-05	NA	NA	NA
Total PAHs/PCBs	0.7	NA	NA	NA

TABLE 14.12
VOC Emission Rate (STPY) for Stickney WRP Targeted VOCs Computed Using Various Noncomprehensive Models[a]

Year	N-R	NCASI	TSDF
1987	16.07	13.76	9.89
1988	29.46	24.92	29.3
1989	95.46	92.34	96.4
1990	18.14	17.11	18.08
1991	11.76	8.74	7.35
1992	11.26	8.76	7.09

[a] Based on analysis of 30 VOCs each year.

The annual VOC emission rates computed by the comprehensive general fate models of WATER7/8, BASTE and TOXCHEM were compared. Similar studies were conducted to compare the annual emission rates of the 14 water pollution control plants owned and operated by the Department of Environmental Protection of New York City.[15] TOXCHEM, WATER8 and BASTE models were used to compute the annual emission rates in these studies. In both studies, direct measurements of VOCs were made to compare the measured emission rates with the model-predicted emission rates. The results of these two major studies are presented and discussed below.

14.5.1 THE METROPOLITAN WATER RECLAMATION DISTRICT OF GREATER CHICAGO STUDIES

MWRDGC conducted extensive studies to compute and compare the annual VOC emission rates for the Stickney, Calumet and North Side WRPs using the WATER7/WATER8, BASTE and TOXCHEM models. The emission rates were obtained using the influent VOC concentrations of these WRPs along with other plant operational parameters as inputs to these various models.

VOC emission estimates were computed by the above models using the WATER7 model compound parameters for stripping or volatilization, sorption and biodegradation. All the input parameters to the models, such as flows, plant operational parameters, unit process configurations, VOC concentration of the influent, effluent, primary sludge and WAS, mixed liquor and suspended solids, were identical. The above models have default coefficient values for stripping or volatilization, sorption and biodegradation of various VOCs. BASTE has the lowest number of default values, whereas the TOXCHEM and WATER7/8 models have a database of default values for a large number of compounds. Models permit the use of coefficients of choice by the user, or default values included in the model can be used. Also, in the case of WATER7/8, when a coefficient is not available for the property of a specific compound, it can be derived based on properties such as structure–activity relationships. Identical plant operating parameters and influent concentrations of selected VOCs were used as inputs to the three models to delineate the similarities and differences in model outputs. However, VOC emission rates for the grit chamber, primary and secondary settling tanks and aeration tank unit processes of the Stickney Water Reclamation Plant were computed using each model with its own compound property parameter values and with those of the other two models. The compounds selected for this comparative study of the models were benzene, chloroform, ethylbenzene, methylene chloride, tetrachloroethene, toluene, trichloroethane, trichloroethene and xylenes. Tables 14.13 through 14.15 present the results.

14.5.1.1 VOC Emission Estimates Computed by WATER7 Model Using the Compound Parameters of the WATER7, BASTE and TOXCHEM Models

WATER7 predicted the highest VOC emissions when BASTE compound parameters were used (40.7 STPY) vs. 29 and 27.6 STPY by WATER7 and TOXCHEM parameters, respectively. This is because the BASTE model assigns biodegradation con-

TABLE 14.13
Stickney WRP VOC Emissions Computed by WATER7

	WATER7 Model (stpy)												
	Grit			Primary			Aeration			Secondary			Total
Organic Compounds	VOL$_{diff}$	VOL$_{strp}$	VOL$_{tot}$	VOL$_{diff}$	VOL$_{weir}$	VOL$_{tot}$	VOL$_{diff}$	VOL$_{strp}$	VOL$_{tot}$	VOL$_{diff}$	VOL$_{weir}$	VOL$_{tot}$	Emissions
						(WATER7 Parameters)							
Benzene	0.033		0.033	0.138	0.008	0.147	0.000	0.028	0.028	0.012	0.000	0.013	0.220
Chloroform	0.192		0.192	0.808	0.043	0.852	0.005	0.216	0.220	0.146	0.002	0.148	1.412
Ethylbenzene	0.231		0.231	0.812	0.057	0.869	0.001	0.147	0.148	0.054	0.001	0.055	1.303
Methylene chloride	0.355		0.355	1.573	0.079	1.651	0.017	0.688	0.706	0.501	0.007	0.507	3.219
Tetrachloroethene	1.154		1.154	3.383	0.478	3.862	0.003	1.273	1.276	0.116	0.001	0.117	6.409
Toluene	0.918		0.918	3.590	0.251	3.841	0.005	0.523	0.528	0.192	0.002	0.194	5.481
Trichloroethane	0.428		0.428	1.623	0.167	1.790	0.004	0.970	0.973	0.149	0.001	0.150	3.341
Trichloroethene	0.202		0.202	0.824	0.062	0.886	0.002	0.322	0.324	0.090	0.001	0.091	1.504
Xylenes	1.053		1.053	3.905	0.242	4.147	0.008	0.630	0.638	0.284	0.004	0.288	6.126
Total	4.564		4.564	16.658	1.387	18.045	0.045	4.796	4.842	1.544	0.019	1.563	29.014
						(BASTE Parameters)							
Benzene	0.033		0.033	0.141	0.009	0.150	0.000	0.003	0.003	0.001	0.000	0.001	0.188
Chloroform	0.183		0.183	0.687	0.039	0.726	0.026	1.597	1.623	0.971	0.016	0.987	3.520
Ethylbenzene	0.227		0.227	0.807	0.055	0.862	0.000	0.034	0.034	0.013	0.000	0.013	1.136
Methylene chloride	0.389		0.389	1.649	0.085	1.735	0.071	3.162	3.233	2.241	0.033	2.273	7.630
Tetrachloroethene	0.886		0.886	1.088	0.237	1.324	0.010	8.033	8.043	0.771	0.021	0.793	11.047
Toluene	0.928		0.928	3.701	0.258	3.959	0.001	0.082	0.083	0.030	0.000	0.030	5.000
Trichloroethane	0.287		0.287	1.121	0.067	1.189	0.031	2.447	2.478	1.134	0.017	1.151	5.105
Trichloroethene	0.214		0.214	0.846	0.068	0.914	0.009	1.549	1.557	0.332	0.004	0.335	3.020

Xylenes	1.025		1.025	0.330	0.025	0.355	0.021	1.835	1.856	0.774	0.011	0.786	4.022
Total	4.173		4.173	10.372	0.842	11.214	0.169	18.742	18.911	6.267	0.102	6.369	40.667
					(TOXCHEM Parameters)								
Benzene	0.033		0.033	0.138	0.009	0.146	0.000	0.006	0.006	0.003	0.000	0.003	0.188
Chloroform	0.155		0.155	0.621	0.030	0.650	0.014	0.410	0.424	0.390	0.007	0.396	1.625
Ethylbenzene	0.230		0.230	0.832	0.058	0.890	0.000	0.046	0.046	0.017	0.000	0.017	1.183
Methylene chloride	0.225		0.225	0.832	0.037	0.869	0.025	0.514	0.539	0.619	0.013	0.633	2.265
Tetrachloroethene	0.883		0.883	3.500	0.292	3.792	0.021	3.472	3.493	0.805	0.009	0.813	8.982
Toluene	0.643		0.643	2.428	0.123	2.551	0.004	0.173	0.177	0.133	0.002	0.136	3.508
Trichloroethane	0.336		0.336	1.335	0.093	1.429	0.005	0.568	0.574	0.192	0.002	0.194	2.533
Trichloroethene	0.185		0.185	0.742	0.050	0.793	0.005	0.496	0.501	0.178	0.002	0.181	1.658
Xylenes	1.064		1.064	4.217	0.253	4.470	0.001	0.078	0.079	0.037	0.000	0.037	5.650
Total	3.753		3.753	14.646	0.945	15.590	0.075	5.764	5.839	2.375	0.036	2.410	27.593

TABLE 14.14
Stickney WRP VOC Emissions Computed by BASTE

	BASTE Model (stpy)												
	Grit			Primary			Aeration			Secondary			Total
Organic Compounds	VOL_{diff}	VOL_{strp}	VOL_{tot}	VOL_{diff}	VOL_{weir}	VOL_{tot}	VOL_{diff}	VOL_{strp}	VOL_{tot}	VOL_{diff}	VOL_{weir}	VOL_{tot}	Emissions
					(WATER7 Parameters)								
Benzene	0.002		0.002	0.006	0.031	0.037			0.017	0.001	0.001	0.002	0.058
Chloroform	0.008		0.008	0.039	0.207	0.245			0.128	0.013	0.014	0.027	0.408
Ethylbenzene	0.013		0.013	0.038	0.188	0.226			0.095	0.005	0.005	0.010	0.345
Methylene chloride	0.015		0.015	0.072	0.380	0.453			0.450	0.045	0.045	0.090	1.008
Tetrachloroethene	0.181		0.181	0.144	0.691	0.834			3.122	0.045	0.041	0.086	4.224
Toluene	0.053		0.053	0.156	0.784	0.940			0.331	0.019	0.018	0.037	1.361
Trichloroethane	0.047		0.047	0.060	0.292	0.352			0.816	0.019	0.018	0.037	1.252
Trichloroethene	0.014		0.014	0.033	0.164	0.197			0.230	0.010	0.009	0.019	0.460
Xylenes	0.051		0.051	0.188	0.969	1.158			0.410	0.030	0.030	0.060	1.678
Total	0.384		0.384	0.736	3.706	4.442			5.600	0.187	0.182	0.369	10.795
					(BASTE Parameters)								
Benzene	0.002		0.002	0.006	0.031	0.036			0.012	0.001	0.001	0.002	0.052
Chloroform	0.008		0.008	0.038	0.203	0.241			1.454	0.152	0.155	0.307	2.009
Ethylbenzene	0.013		0.013	0.038	0.188	0.226			0.109	0.006	0.006	0.012	0.360
Methylene chloride	0.011		0.011	0.073	0.411	0.484			2.335	0.335	0.361	0.696	3.526
Tetrachloroethene	0.099		0.099	0.141	0.687	0.828			9.099	0.238	0.222	0.460	10.487
Toluene	0.055		0.055	0.154	0.771	0.925			0.287	0.016	0.015	0.031	1.297
Trichloroethane	0.046		0.046	0.056	0.271	0.327			4.038	0.090	0.084	0.175	4.585
Trichloroethene	0.014		0.014	0.035	0.175	0.210			1.813	0.088	0.084	0.172	2.208
Xylenes	0.055		0.055	0.181	0.913	1.094			0.325	0.021	0.020	0.041	1.516
Total	0.303		0.303	0.721	3.649	4.370			19.471	0.946	0.949	1.894	26.039

(TOXCHEM Parameters)										
Benzene	0.002	0.002	0.006	0.031	0.037	0.004	0.000	0.000	0.000	0.043
Chloroform	0.005	0.005	0.034	0.194	0.229	0.247	0.037	0.040	0.076	0.557
Ethylbenzene	0.013	0.013	0.038	0.188	0.226	0.028	0.002	0.002	0.003	0.270
Methylene chloride	0.007	0.007	0.055	0.324	0.380	0.275	0.052	0.059	0.111	0.774
Tetrachloroethene	0.073	0.073	0.139	0.681	0.820	3.229	0.115	0.108	0.223	4.345
Toluene	0.024	0.024	0.134	0.723	0.857	0.096	0.011	0.012	0.023	1.000
Trichloroethane	0.021	0.021	0.057	0.284	0.341	0.394	0.020	0.020	0.040	0.795
Trichloroethene	0.011	0.011	0.032	0.162	0.194	0.364	0.020	0.020	0.040	0.609
Xylenes	0.054	0.054	0.204	1.051	1.255	0.048	0.004	0.004	0.007	1.363
Total	0.210	0.210	0.699	3.639	4.338	4.684	0.261	0.263	0.525	9.757

TABLE 14.15
Stickney WRP VOC Emissions Computed by TOXCHEM

	TOXCHEM Model (stpy)													
	Grit			Primary			Aeration			Secondary			Total
Organic Compounds	VOL_{diff}	VOL_{strp}	VOL_{tot}	VOL_{diff}	VOL_{weir}	VOL_{tot}	VOL_{diff}	VOL_{strp}	VOL_{tot}	VOL_{diff}	VOL_{weir}	VOL_{tot}	Emissions
						(WATER7 Parameters)							
Benzene	0.000	0.000	0.001			0.022	0.001	0.029	0.030			0.001	0.054
Chloroform	0.003	0.001	0.004			0.155	0.011	0.211	0.222			0.018	0.399
Ethylbenzene	0.002	0.001	0.003			0.101	0.003	0.126	0.129			0.005	0.238
Methylene chloride	0.007	0.002	0.009			0.373	0.043	0.716	0.759			0.071	1.212
Tetrachloroethene	0.009	0.027	0.036			0.447	0.026	3.830	3.856			0.041	4.380
Toluene	0.010	0.007	0.017			0.491	0.013	0.523	0.536			0.021	1.065
Trichloroethane	0.004	0.007	0.011			0.196	0.012	1.159	1.171			0.019	1.397
Trichloroethene	0.002	0.002	0.005			0.118	0.007	0.363	0.370			0.011	0.503
Xylenes	0.010	0.006	0.016			0.492	0.017	0.538	0.555			0.025	1.088
Total	0.048	0.054	0.103			2.394	0.132	7.495	7.627			0.213	10.337
						(BASTE Parameters)							
Benzene	0.000	0.000	0.001			0.022	0.000	0.004	0.004			0.000	0.026
Chloroform	0.003	0.001	0.004			0.155	0.074	1.412	1.486			0.119	1.765
Ethylbenzene	0.002	0.001	0.003			0.101	0.001	0.029	0.030			0.001	0.135
Methylene chloride	0.007	0.002	0.009			0.373	0.177	2.969	3.147			0.297	3.826
Tetrachloroethene	0.008	0.010	0.018			0.406	0.087	6.236	6.324			0.140	6.888
Toluene	0.010	0.007	0.018			0.491	0.002	0.084	0.086			0.003	0.598
Trichloroethane	0.004	0.002	0.006			0.193	0.082	2.346	2.427			0.128	2.754
Trichloroethene	0.002	0.003	0.005			0.119	0.028	1.915	1.943			0.046	2.114
Xylenes	0.000	0.000	0.000			0.177	0.000	0.007	0.007			0.001	0.185
Total	0.038	0.028	0.065			2.037	0.452	15.002	15.454			0.735	18.291

				(TOXCHEM Parameters)					
Benzene	0.000	0.000	0.001	0.021	0.000	0.006	0.007	0.000	0.029
Chloroform	0.003	0.001	0.004	0.142	0.029	0.348	0.377	0.045	0.569
Ethylbenzene	0.002	0.002	0.004	0.108	0.001	0.043	0.044	0.002	0.158
Methylene chloride	0.007	0.001	0.008	0.318	0.061	0.418	0.480	0.094	0.899
Tetrachloroethene	0.009	0.010	0.019	0.435	0.059	3.871	3.930	0.094	4.478
Toluene	0.010	0.003	0.013	0.451	0.009	0.151	0.160	0.014	0.638
Trichloroethane	0.004	0.003	0.007	0.189	0.014	0.583	0.597	0.022	0.815
Trichloroethene	0.002	0.002	0.004	0.111	0.013	0.491	0.504	0.021	0.640
Xylenes	0.011	0.006	0.018	0.531	0.002	0.072	0.075	0.004	0.627
Total	0.049	0.027	0.076	2.307	0.189	5.984	6.173	0.295	8.851

stant value of zero to chloroform, methylene chloride, tetrachloroethene, trichloroethene, trichloroethane and xylenes. Whatever VOC losses occurred in reality due to biodegradation obviously were accounted for by mechanisms other than biodegradation. Since adsorption losses of VOCs were usually minimal, the fate of these VOCs was accounted for by volatilization losses in these computations. This is exemplified further by the fact that all the models gave the highest volatilization losses from aeration tanks when BASTE default parameter values were used (18.9, 19.5 and 15.5 STPY) with the WATER7, BASTE and TOXCHEM models, respectively. In contrast, VOC losses due to volatilization from aeration tanks ranged from 4.68 to 7.63 STPY with all models, including the BASTE model, when WATER7 and TOXCHEM compound parameter values for biodegradation were used.

The WATER7 model (with its own default parameter values) predicted a total of 29 STPY for VOC emissions from all unit processes. Of these, 24.2 STPY of the emissions were from grit chambers and primary and secondary clarifiers. WATER7 also predicted significantly higher VOC emissions from primary clarifiers, not only with its own default parameter values, but also with those of the BASTE and TOXCHEM models (18.0, 11.2 and 15.6 STPY) in contrast to the VOC losses in the range of 2.04 to 4.45 STPY predicted by the BASTE and TOXCHEM models using compound parameter values of any of the models. Most of the volatilization losses from the primary and secondary clarifiers were attributable to diffusion rather than weir drop.

14.5.1.2 VOC Emission Estimates Computed by the BASTE Model Using the Compound Parameters of the WATER7, BASTE and TOXCHEM Models

The highest VOC emission rate of approximately 26.1 STPY occurred for all the comparisons made in this study when this model was used with its own default parameter values. The corresponding VOC estimates using the WATER7 and TOXCHEM parameters were 10.8 and 9.8 STPY, which were comparable. The higher VOC emission estimates with the BASTE model using its own default parameter values is presumably due to an underestimation of the biodegradation of several VOCs, as biodegradation constants for these compounds have a value of zero, as mentioned previously.

A significant proportion of the volatilization losses in the primary and secondary clarifiers could be attributed to weir drop when computed by the BASTE model. This was opposite to the results of the TOXCHEM model, in which diffusion was the main mechanism.

14.5.1.3 VOC Emission Estimates Computed by the TOXCHEM Model Using the Compound Parameters of the WATER7, BASTE and TOXCHEM Models

VOC emission rates were comparable with WATER7 and TOXCHEM default compound parameter values (10.32 and 8.39 STPY). These emission rates were considerably lower than the estimates derived using the BASTE model's compound parameter values. Once again, this is presumably attributable to an underestimation of the losses due to biodegradation of several VOCs. TOXCHEM yielded the lowest primary clarifier VOC emission rates with the compound parameter values of all the models in comparison with the emission estimates of the WATER7 and BASTE models, either with their own default parameter values or with those of the other models.

14.5.1.4 Comparison of Directly Measured VOC Emission Rates and Model-Predicted VOC Emission Rates

As can be seen from the foregoing results, VOC emission rate estimates were obtained in the range of 8.9 to 40.7 STPY for the Stickney WRP, depending on which models and compound parameter values were used.

Two separate experimental runs were also conducted at the Stickney WRP in which directly measured annual VOC emission rates were compared with those predicted by the above three mathematical models. Offgas from the grit chambers and the aeration tanks were collected into Suma canisters using the flux chamber technique and the concentrations of VOCs detected were measured.[20] The emission rates were computed using the U.S. EPA's WATER8,[21] BASTE and TOXCHEM+ [22] models. The models were applied using the influent VOC concentrations to the grit chamber. For the TOXCHEM+ and WATER8 models, default compound parameter values for volatilization, sorption and biodegradation from their respective databases were used. Since the BASTE model did not have parameter values for a number of the compounds, the WATER8 parameter values were used as default values. The annual emission rates were computed for each of the wastewater treatment processes. The models were also applied to compute annual emission rates from the aeration basins based upon the influent VOC concentration to the aeration basin. To determine how close the model-predicted and directly measured VOC emission rates were, the percent relative error for each of the three model estimates, with respect to the directly measured rate, was computed [[(Percent relative error = [(model-predicted emission rate) – (directly measured emission rate)/(directly measured emission rate)] × 100]].

In these studies, it was found that the directly measured VOC emission rate at the Stickney WRP was lower than the rate predicted by the WATER8 model in the first run. In the second run, the directly measured VOC emission rate was higher than the predicted rates of all three models. The directly measured VOC emission rates of four compounds, i.e., chloroform, methylene chloride, tetrachloroethylene and trichloroethylene accounted for the major part of the VOC emissions (97.4% in the first run and 91.4% in the second).

The WATER8 model-predicted values for the Stickney aerated grit chambers had the highest percentage of errors, averaging 1.386%. Both the BASTE and TOXCHEM+ models underestimated the emissions at the Stickney WRP grit chamber, averaging −10.8 and −17.4, respectively. A similar comparison was made at another water reclamation plant. These two models overestimated the grit chamber emissions, averaging 85.6 and 56.1% relative errors, respectively.

Although the BASTE and TOXCHEM models predicted higher emissions than actually observed, they yielded emission rates closer to the directly measured emission rates than the WATER8 model.

Tata et al.[23] also compared directly measured VOC emission rates of six California POTWs with emissions predicted by the above three mathematical models. From these studies, it was concluded that the total VOC emission rates predicted by the WATER7, BASTE and TOXCHEM models for the most part were considerably higher than the directly measured VOC emission rates. Depending on which combination of model and model compound parameter values was used, VOC emission rates predicted by these models were 176.4 to 1667.4% higher than the directly measured VOC emission rates; the WATER7 model always yielded the most conservative VOC emission rates, either with its own default compound parameter values or with those of the other models.

In the case of one POTW, directly measured emission rates were higher than the VOC emission rates predicted by all three models with TOXCHEM and WATER7 model compound parameter values. At this POTW, the directly measured emission rates of 1,1,1-trichloroethane and chloroform were considerably higher than the model-predicted emission rates for these compounds and contributed to the overall higher value for the directly measured VOC emission rate compared with the predicted emission rate. The higher chloroform emission rate measured by direct measurements can be attributed to the formation of chloroform in a scrubber, where hypochlorite was used.

In addition, the directly measured VOC emission rates of the above two compounds, which were higher than the model-predicted emission rates, were likely due to a difference in the times of sampling the influent for VOC concentrations (for model prediction of emission rates) and sampling the air emissions (for direct measurement of VOC emission rates). It is likely that a wastewater stream containing a high concentration of 1,1,1-trichloromethane passed through the plant at the time air samples were collected. Hence, for model calibration, it is important to collect samples of the influent and air over the unit wastewater treatment processes in a time sequence that would correspond to each other specified for the characterization of a major source.

14.5.2 THE NEW YORK CITY DEPARTMENT OF ENVIRONMENTAL PROTECTION STUDIES

As indicated previously, Malcolm Pirnie Inc., White Plains, NY and the Illinois Institute of Technology, Chicago jointly conducted detailed studies to determine the annual VOC emissions of New York City's 14 water pollution control plants (WPCPs), namely, Wards Island, North River, Rockway, 26th Ward, Bowery Bay, Hunts Point, Jamaica, Newton Creek, Oakwood Beach, Red Hook, Port Richmond, Tallman Island and Owls Head. The Owls Head plant was under construction and was not included in the study. All these plants are operated by the New York City of Department of Environmental Protection. The major objectives of the study were to:

- Estimate the annual VOC emissions of the WPCPs and determine whether they are major sources of VOC emissions

- Determine the level of worker exposure to the VOC emissions within the boundaries of the WPCPs
- Evaluate impacts of VOC emissions on public health of the communities surrounding the WPCPs

In general, the unit processes of all of the WPCPs include headworks (bar screens and grit tanks), primary sedimentation tanks, biological treatment (step-feed aeration tanks, except for Newton Creek for which a plug-flow system was simulated), secondary settling tanks, disinfection (chlorine contact tanks and associated effluent weirs), wastewater channels and sludge handling (gravity thickeners and anaerobic digesters). Appropriate unit processes and wastewater characteristics were used with the TOXCHEM model to predict VOC emissions from the various WPCPs. Annual emission rates using the directly measured VOCs were computed and compared with the model predicted emission rates. Also, as in the Chicago study, VOC emissions were estimated for the Wards Island WPCP (flow: 265 mgd) by each of the TOXCHEM+, BASTE and WATER8 models with their own individual default parameters and with parameters of the other two models to compare the model outputs.

Table 14.16 gives the results reported from this study. Except in the case of Red Hook WPCP, all the modeled emissions were considerably higher than the directly measured emission rates, thereby indicating the conservative nature of the model in predicting the VOC emissions.

Tables 14.17 through 14.19 present a comparison of the predicted emissions of total VOCs, chlorinated VOCs (bromodichloromethane, cis(1,2) dichloroethene, methylene chloride, terachlotrichloroethene) and nonchlorinated VOCs (benzene, toluene and xylenes) by the WATER8, BASTE and TOXCHEM+ models with their individual default parameters and parameters of the other two models against which each of the models is compared. The total VOC emissions included emissions from the primary and secondary settling tanks and aeration tanks.

The emission rates of chlorinated compounds and total VOCs from the aeration tanks predicted by each of the models using BASTE default parameter values were higher than those predicted using WATER8 and TOXCHEM+ default parameters (Table 14.18). This is attributed to the zero biodegradation constants of chlorinated compounds provided by the physico-chemical property compounds of BASTE database. Emission rates of chlorinated VOCs from aeration tanks predicted by WATER8 were higher than from primary or secondary clarifiers because stripping was the dominating mechanism for such compounds and because the turbulence caused by aeration enhances volatilization. The emission rates of nonchlorinated biodegradable VOCs predicted by BASTE and TOXCHEM+ were higher (Table 14.19) from the primary clarifiers than from the aeration tanks because a major fraction of these VOCs were biodegraded in the aeration tanks.

The specific model or model parameter combinations that predicted the highest and lowest emission rate for eight of the most commonly occurring VOCs in POTW influents of the NYCDEP WPCPs are presented in Table 14.20. WATER8 model yielded seven of the eight highest estimates; the highest VOC estimates for all these VOCs resulted when WATER8 was used with BASTE default parameters. This may be attributable to the higher values of the Henry's Law constants provided by the

TABLE 14.16
Model Predicted and Directly Measured VOC Emission Rates of New York City Department of Environmental Protection WPCPs*

WPCP	VOC Emissions Based on Model (tons/yr)**	VOC Emissions Based on Direct Measurements (tons/yr)
26th Ward	4.81	1.59
Bowery Bay	2.70	1.33
Hunts Point	3.32	0.95
Jamaica	3.21	0.57
Newton Creek	12.70	2.89
Oakwood Beach	1.15	0.46
Port Richmond	1.45	0.32
Red Hook	0.75	0.95
Tallman Island	2.07	0.80
North River	4.33	1.01
Rockaway	2.48	0.11
Wards Island	15.70	2.82

* Source: Malcolm Pirnie and Illinois Institute of Technology, Analysis of Volatile Organic Compound Emissions from the New York City Wastewater Collection Treatment System, Vol. 2: Aeration Tank Emissions of Volatile Organic Compounds from the New York City Department of Environmental Protection Water Pollution Control Plants

** TOXCHEM+

model for these VOCs. The lowest emission rates were predicted by the BASTE model for seven VOCs when it was used with WATER8 or TOXCHEM+ model default values. Statistical analyses also indicated that the WATER8 model predicted the highest VOC emission rates among the three models examined.

The higher emission rates generally predicted by theWATER7/8 model are due to conservative mass transfer kinetics. Ferro and Pincince,[24] in an evaluation of the mechanisms used by the three models, explain the differences in emission rates observed as being due to differences in the calculation of the liquid phase mass transfer coefficient (K_2). BASTE and TOXCHEM calculate K_2 as a function of wind speed and diffusivity, whereas WATER7/8 uses a modification of the reaeration function developed by Owens et al.[25] Also, the generally conservative nature of all models is attributable to the choice of inappropriate algorithms and coefficients for the volatilization and biodegradation components of the models. The liquid phase mass transfer coefficients used by WATER8 were an order of magnitude higher than those calculated from tracer field data.[26,27]

TABLE 14.17
Comparison of Total VOC Emissions Predicted With Various Models with their Individual Default Parameters and Parameters of Other Models

Scenario (Model/Parameters	Primary Settling Tanks (lb/d)	Aeration Tanks, (lb/d)	Final Settling Tanks (lb/d)	Total lb/d
WATER8/WATER8	10.332	16.727	1.329	28.388
WATER8/BASTE	9.513	19.628	1.455	30.596
WATER8/TOXCHEM+	9.891	17.703	1.216	28.810
BASTE/WATER8	3.087	2.363	1.896	7.346
BASTE/BASTE	3.002	6.048	4.111	13.161
BASTE/TOXCHEM+	3.081	3.156	2.495	8.732
TOXCHEM+/WATER8	4.820	3.497	1.556	9.872
TOXCHEM+/BASTE	4.823	6.836	2.848	14.506
TOXCHEM+/ TOXCHEM+	4.791	4.287	1.947	11.025

TABLE 14.18
Comparison of Chlorinated VOC Emissions Predicted With Various Models with their Individual Default Parameters and Parameters of Other Models

Scenario (Model/Model Parameters Used)	Primary Settling Tanks (lb/d)	Aeration Tanks (lb/d)	Final Settling Tanks (lb/d)	Total lb/d
WATER8/WATER8	19.9	34.4	2.72	57.02
WATER8/BASTE	17.1	45.81	3.32	66.23
WATER8/TOXCHEM+	18.6	40.3	2.81	61.71
BASTE/WATER8	5.9	5.9	4.52	16.32
BASTE/BASTE	5.63	17.8	11.72	35.15
BASTE/TOXCHEM+	5.8	8.72	6.9	21.42
TOXCHEM+/WATER8	9.4	8.9	3.64	21.94
TOXCHEM+/BASTE	9.4	19.6	7.94	36.94
TOXCHEM+/ TOXCHEM+	9.3	11.91	5.36	26.57

TABLE 14.19
Comparison of Non-Chlorinated VOC Emissions Predicted with Various Models with their Individual Default Parameters and Parameters of Other Models

Scenario (Model/Parameters)	Primary Settling Tanks (lb/d)	Aeration Tanks, (lb/d)	Final Settling Tanks (lb/d)	Total lb/d
WATER8/WATER8	12.9	18.7	1.5	33.1
WATER8/BASTE	13.1	16.5	1.3	30.9
WATER8/TOXCHEM+	12.8	15.9	1.05	29.75
BASTE/WATER8	3.9	1.6	1.5	7
BASTE/BASTE	3.9	1.4	1.33	6.63
BASTE/TOXCHEM+	3.98	1.3	1.02	6.3
TOXCHEM+/WATER8	5.9	2.2	1.3	9.4
TOXCHEM+/BASTE	5.91	2.1	1.1	9.11
TOXCHEM+/ TOXCHEM+	5.91	1.7	0.82	8.43

TABLE 14.20
Model-Model Default Parameter Combinations Predicting Highest and Lowest Emission Rates for VOCs Commonly Found In POTW Influents

VOC	Lowest Emission Rate Estimate (Model/Parameters)	Highest EmissionRate Estimate (Model/Parameters)
Benzene	BASTE/TOXCHEM+	WATER8/WATER8
Chloroform	BASTE/WATER8	WATER8/BASTE
Cis(1,2)Dichloroethene	BASTE/WATER8,TOXCHEM+	WATER8/BASTE
Methylene chloride	BASTE/WATER8	WATER8/BASTE
Toluene	BASTE/WATER8	WATER8/BASTE
Tetrachloroethene	BASTE/TOXCEHEM+	WATER8/BASTE
Trichloroethene	TOXCHEM+/TOXCHEM+	BASTE/BASTE, WATER8
Xylenes	BASTE/TOXCHEM+	WATER8/WATER8
Total VOCs	BASTE/WATER8	WATER8/BASTE

14.6 SUMMARY

The wide range of emission rate values predicted by the general fate models with their own and other models' default parameters for a given water reclamation plant (WRP) suggests that the use of models to characterize a WRP as a major source using the CAAA 1990 Title III definition is not reliable. Models, however, can be used for screening purposes. Due to their highly conservative nature, if the annual emission rates of POTWs computed by the models are less than the limits specified for major sources, it is safe to assume that the POTWs are not major sources. However, if the model-computed annual VOC emission rate is above the specified major source limits, it is prudent to make direct measurements to ascertain whether a POTW is a major source. It is highly unlikely that a POTW will be a major source in reality, if the model-computed annual emission rate is marginally above the limits. The higher emission rates generally predicted by the WATER7/8 model are due to conservative mass transfer kinetics.

REFERENCES

1. James M. Montgomery Consulting Engineers Inc., Joint Powers Agencies for Pooled Emission Estimation Program (PEEP), Final Report for Publicly Owned Treatment Works (POTWs), Pasadena, California, 1990.
2. CH2M HILL, JEIP (Joint Emissions Inventory Program) SCAQMD Rule 1179 Emissions Inventory Report, Vol I., Oakland, California, 1993.
3. TriTAC in Collaboration with California POTWs and Air Quality Regulatory Agencies, Guidance Document on Control Technology for Air Emissions from POTWs, 1984.
4. Bell, J.P., Monteith, H., Parker, W.J., Melcer, H., Corsi, R.L. and Zytner, R., Modeling the Stripping and Volatilization of VOC in Wastewater Collection and Treatment Systems, Water Environment Research Foundation Project 91-TFT-1, Alexandria, Virginia, 1998.
5. Caballero, R., VOC emissions from POTWs, Appendix I, paper presented at the Joint U.S. EPA/WPCF Workshop on Air toxics Emissions and POTWs, Alexandria, Virginia, 1989.
6. Namkung, E. and Rittmann, B.E., Estimating volatile organic compound emissions from publicly owned treatment works, *J. Water Poll. Contr. Fed.*, 59: 670–678, 1987.
7. Noll, K E. and De Paul, F.T., Emission of volatile organic compounds from the sewage treatment facilities of the Metropolitan Sanitary District of Greater Chicago, Appendix P, Proc. Water Pollution Control Federation/U.S. EPA Workshop: Air Toxics Emissions and POTWs, 1990.
8. Barton, D.A., Organic Compound Elimination Pathway Model, Version 1.34, National Council for Air and Stream Improvement (NCASI), 1998.
9. U.S. EPA, Hazardous Waste Treatment, Storage and Disposal Facilities (TSDF), Air Emission Models, EPA Report No. 450/3-87-026, 1987. www.epa.gov/ttn/catc/products.html#rblcdocs,
10. Eyma, R.R., Estimation of volatile organic compound emissions from activated sludge and secondary clarification units, Poster Paper (Metcalf and Eddy, Inc.) Presented at Annual Water Environment Federation Conference, 10 pp, 1992.
11. Monteith, H.D., Balogh, S., Parker, W.J. and Yendt, C.M., Modeling VOC emissions from a POTW. Presented at the Annual Water Environment Federation Conference, Miami Beach, Florida, 295–303, 1995.
12. Melcer, H., Parker, W.J. and Monteith, H., Estimating emissions of toxic pollutants, *Water Environ. Technol.*, 50–56, 1994.
13. Sajjad, A., Gluckmman, J., Barney, J, Cchaiken, S., Tata, P. and Lue-Hing, C., Trends in reduction of toxic pollutants. Presented at the 75th Annual Water Environment Federation Conference and Exposition, New Orleans, Louisiana, 1999.

14. Wolstenholme, P.L. and Finger, R., Air toxics modeling and control at a large wastewater treatment works. Presented at the Air and Waste Management Association Annual Conference, 1993.
15. Malcolm Pirnie Inc. and Illinois Institute of Technology, Analysis of Volatile Organic Compound Emission from the New York City Wastewater Collection/Treatment System, Vol. 3, General Fate Modeling of Volatile Organic Compounds at the New York City Department of Environmental Protection Water Pollution Control Plants, New York City Department of Environmental Protection, 1999.
16. Hentz et al. personal communication, 2000.
17. Mayer, G.J., Cheng, I.S., Pau, P. and Mohamed, F., Emissions of air toxics from wastewater treatment plants, *Water Env. Res.*, 66: 140, 1994.
18. Tata, P., Soszynski, S., Zenz, D.R., Lordi, D.T. and Lue-Hing, C., Volatile organic compound emissions from the water reclamation plants of the Metropolitan Water Reclamation District of Greater Chicago. Presented at the Water Environment Federation Specialty Conference on Control of Emissions of Odors and Volatile Organic Compounds, Jacksonville, Florida, 1994.
19. Schroy, J.M., Evaluation of emissions from wastewater treatment systems — a comparison of available software performance. Presented at the AIChE Annual Summer National Meeting, 1994.
20. Tata, P., Lordi, D.T., Soszynski, S., Zenz, D.R. and Lue-Hing, C., Emission of Volatile Organic Compounds from the Water Reclamation Plants of the Metropolitan Water Reclamation District of Greater Chicago, Report No. 98-30, Research and Development Department, Metropolitan Water Reclamation District of Greater Chicago, 1998.
21. U.S. EPA Users Guide for Wastewater Treatment Compound Property Processor and Air Emissions Estimator (WATER8, EPA Report 453C) 94-080C, Nov. 1994.
22. Enviromega, Inc., Users' Manual, Toxic Chemical Modeling Program for Water Pollution Control Plants (TOXCHEM+), Version 1, Enviromega, Dundas, Ontario, 1994.
23. Tata, P., Soszynski, S., Lordi, D.T., Zenz, D.R., Lue-Hing, C. and Card, T., Prediction of volatile organic compound emissions from Publicly Owned Treatment works, *Proc. 68th Annual Water Environment Federation Conference*, Miami Beach, Florida, 1995.
24. Ferro A.R. and Pincince, A.B., Comparison of computer programs for estimating emissions of volatile organic compounds from wastewater treatment facilities, paper presented 1992 Annual Conference and Exposition of the Water Environment Federation, Dallas, 1992.
25. Owens, M., et al. Some reaeration studies in streams. *J. Int. Water Pollut.* 8: 469, 1964.
26. American Petroleum Institute, Health and Environmental Sciences Department. A Fundamental Evaluation of the CHEMDAT7 Air Emissions Model, Publication No. 4571, 1993.
27. Rajagopalan, S., Meyer, C.L., Rhodes, I.A., Sun, P.T., van Compernolle, R., Walker, S., Scott, R.R. and Claybon, R.W. Comparison of methods for determining biodegradation kinetics of colatile organic compounds. Presented at Water Environment Federation 67th Annual Conference, Chicago, 1994.
28. U.S. EPA, User's Guide for WATER9 Software, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 2001. Water Environment Federation/U. S. Environmental Protection Agency (1989). Workshop Report and Proceedings: Air Toxics Emissions and POTWs, 1989.
29. Wisner, C.E. and Davis, T.W., Characterization of fugitive emission rates using a mobile integrating sampler, Proc. 1989 EPA/AWMA Symposium on Measurement of Toxic and Related Air Pollutants, Raleigh, North Carolina, 1989.

15 Control Technologies

Jay Witherspoon, Prakasam Tata,
Tom Card and Cecil Lue-Hing

CONTENTS

15.1 Introduction 316
15.2 Overview of Control Technologies 316
    15.2.1 Traditional Vapor Phase Controls 316
    15.2.2 Nontraditional Vapor Phase Controls 317
    15.2.3 Containment 317
    15.2.4 Process and Practice Modifications 320
    15.2.5 Source Control 321
15.3 Comparison of Control Technologies 321
    15.3.1 Traditional Vapor Phase Controls: Thermal Treatment 321
    15.3.2 Incinerators 323
    15.3.3 Flares 323
    15.3.4 Recuperative Oxidizers 325
    15.3.5 Regenerative Oxidizers 327
    15.3.6 Catalytic Incinerators 329
    15.3.7 Wet Scrubbing 330
    15.3.8 Packed-Tower Scrubbers 332
    15.3.9 Mist Scrubbers 333
    15.3.10 Dry Chemical Scrubbing 335
    15.3.11 Carbon Adsorption 335
    15.3.12 Biofiltration 337
        15.3.12.1 Process and Its Variations 338
        15.3.12.2 Performance: Factors and Expectations 339
            15.3.12.2.1 Media 340
            15.3.12.2.2 Nutrients 342
            15.3.12.2.3 Microorganisms 342
            15.3.12.2.4 Compounds 342
            15.3.12.2.5 Costs 342
        15.3.12.3 Applicability to POTWs 343
15.4 Summary 344
References 345

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

15.1 INTRODUCTION

As discussed in Chapter 2, air quality regulations will, in some instances, require that emissions from wastewater treatment plants be controlled. In addition, the regulations often will, at a minimum, require control technologies to be evaluated to determine their technical feasibility and cost effectiveness. This chapter summarizes the technologies available to control emissions from POTWs. It includes an overview of control technologies, criteria for evaluation and rating and summaries of performance of each major technology category. This information can be used as part of a cost effectiveness evaluation required when a control technology standard such as best available control technology (BACT) must be applied. This evaluation process is described in Chapter 16. Control technologies can also be used to reduce emissions to avoid certain regulatory and permitting requirements.

15.2 OVERVIEW OF CONTROL TECHNOLOGIES

The control technologies potentially available to POTWs for controlling emissions have been divided into five categories based on the control technique:

1. Traditional vapor phase controls
2. Nontraditional vapor phase controls
3. Containment
4. Process and practice modifications
5. Source control

This chapter primarily addresses control of VOCs from liquid wastewater processes, but also includes information regarding control of emissions of criteria pollutants from combustion processes unique to POTWs. More detailed information regarding control of criteria pollutants is available in other references. Several of the technologies described in this chapter have found their application at POTWs for odor control and not specifically for VOC control. These are activated carbon adsorbers, absorption towers and biofilters.[1-4]

15.2.1 TRADITIONAL VAPOR PHASE CONTROLS

This group of control technologies includes the processes commonly used in the past by other industries for VOC control.[5] These processes, which include thermal oxidation processes and activated carbon adsorption processes, are normally very expensive for treating the typically low concentrations of VOCs associated with the large volume of air usually vented from most wastewater liquid and solids processes. They are usually cost effective only for treating more concentrated air streams such as incinerator emissions. In addition, experience with these processes at POTWs is limited and there is some concern about corrosion and performance in water vapor-saturated gas streams that can contain sulfur and chlorine compounds.

15.2.2 NONTRADITIONAL VAPOR PHASE CONTROLS

Nontraditional vapor phase control technologies include containment by covers, biofilters, atomized mist scrubbers, packed tower scrubbers, IC engines, nonselective oxidizing agents such as ozone and hydrogen peroxide and ultraviolet radiation.[5–8] These technologies have typically been used to control odorous compounds, but have also been shown to be effective in controlling some types of VOC emissions. However, as a group, they still should be considered somewhat experimental for controlling VOCs. With additional research and development, these technologies could be made effective for control of some types of VOCs. The cost of these controls would likely be substantially less than the traditional vapor phase control and they are, in general, more applicable to the dilute VOC air streams collected from POTW liquid processes.

15.2.3 CONTAINMENT

VOCs in wastewater processes that do not openly exhaust to the ambient atmosphere can be prevented from being emitted to the atmosphere by covering the processes or containing them in tanks or vessels. Containing processes can also be used in conjunction with treatment systems. Containment is a passive technology, consumes no energy and does not deliberately vent the emissions to the atmosphere. It has been used successfully at POTWs to control VOC emissions, but not in all configurations.

The types of covers include fixed roof, floating (flexible and rigid) fixed covers in contact with the liquid surface, floating hollow spheres and air-supported structures consisting of an inflated plastic reinforced fabric shell anchored in place. A summary of the factors that govern the performance of covers is given in Table 15.1.[5]

Covering treatment process units may cause the VOCs to remain in solution, only to be emitted in downstream processes unless the downstream processes can remove the VOCs (as biological systems are capable of removing degradable VOCs by oxidation). In addition, in covered systems, the concentration of potentially explosive and toxic compounds can build up and create a safety hazard, especially if operators are required to routinely enter the enclosed area. In pure-oxygen-activated sludge systems, an air automatic explosive detection and air-purge system is included to prevent explosive and fire hazard conditions. This is provided more because of the pure oxygen used, which could support a fire, rather than to contain VOCs. Some unit processes may not be able to be retrofitted with covers due to inadequate wall support.

The efficiency of rigid floating covers is reported to be above 90% and the actual VOC removal efficiency depends on the amount of fugitive emissions from seams and seals of the covers. The removal efficiency of flexible floating covers depends on the permeability of the cover material, fugitive emissions from seams and degradation of the cover materials due to weather and wastewater constituents. Their efficiency is reported to be about 85%. Information on the efficiency of fixed covers in contact with the liquid surface is relatively sparse and their use in wastewater treatment plants is limited, as they require relatively constant water depths, which is not usually the case. Air-supported structures will reduce air emissions by 95%.

TABLE 15.1
Summary of Findings on Different Types of Covers for Controlling VOC Emissions from POTWs

	Covers					
Factor	**Fixed (not in contact with liquid surface)**	**Fixed (in contact with liquid surface)**	**Rigid Floating**	**Flexible Floating**	**Air Supported**	**Floating Hollow Spheres**
VOCs (Range %)	100	100	100	100	Most VOCs dependent on abatement device added	100
Concentration (Range %)	100	100	100	100	11	100
Removal (Range %)	90–95	90	85–90	90–98	41–95 (depends on VOC)	70–91
Interferences	Fugitive emissions from seams, ports and seams	Fugitive emissions flight scrapers	Fugitive emissions from seams, ports and seals	Fugitive emissions from seams, ports and seals	Fugitive emissions from seams, ports and seals	High flow rate and wind increases volatilization
Operational Problems	Corrosion, weathering of seams, ports and seals, Maintenance difficulties					
	Degradation of cover, maintenance difficulties	Degradation of seam and seals	Degradation of seam and seals	Degradation of seam and seals	Maintenance difficulties	
Adaptability to POTWs	Easily adaptable, in use for odor control	Adaptable, must have constant flow rates	Easily adaptable	Easily adaptable, but requires constant head	Limited	Limited: cannot be used for aerated and skimmed processes

Complexity	Simple	Simple, requires constant head	Relatively simple	Relatively simple	More complex than other covers due to inflation	Low
Water Impacts	Entrainment of VOCs, may disrupt downstream operations	Low	Entrainment of VOCs, may disrupt downstream operations	Low	Entrainment of VOCs, may disrupt downstream operations	Entrained VOCs may cause downstream opertional problems
Cross Media Impacts	Possibility of changes in sludge composition		Possibility of changes in sludge composition	Entrainment of VOCs, may disrupt downstream operations	Negligible	Used spheres may pose a hazardous waste disposal problem
Energy Costs	No energy needed	No energy needed	No energy needed	No energy needed	Requires more energy for inflation to operate coolers in warm weather	No energy needed
Total Costs	\$13–\$26/ft^2 covered	\$20–\$30 for rigid floating covers	\$56/ft^2	\$20–\$30 for rigid floating covers; \$3 - \$17/ft^2 for flexible floating covers	\$54–\$65/ft^2, high annual energy costs	\$4.19–\$12.71 per sq. ft., depending on diameter

Source: Bishop, W., Witherspoon, J., Card, T., Chang, D.P.Y. and Corsi, R., Vapor Phase Control Technology Assessment, Water Pollution Control Federation Research Foundation, Virginia, 1990.

Similar to the other covers, they are susceptible to weather, wastewater constituents and sulfuric acid formed through oxidation of hydrogen sulfide. Floating spheres reduce emissions by about 90% and are known to reduce evaporative losses from crude oil plants in the range of 70 to 90%.[9]

Also, covering systems can dramatically accelerate corrosion rates underneath the covers. To avoid this problem, all exposed surfaces under the cover could be coated or replaced with a corrosion resistant material. Containment alone, without scrubbing, will control compounds that are water soluble, such as ethanol. However, controlling highly volatile compounds, such as benzene, will require tight covers or positive ventilation.

To prevent leakage of contaminated air, a ventilation rate sufficient to maintain a negative pressure beneath the covers must be provided. Ventilation rates for covered aeration basins must, at a minimum, be equal to the aeration rate to ensure a negative pressure to prevent leakage. To prevent excessive concentrations of corrosive and explosive gases, 6 to 12 air changes per hour in the headspace between the liquid and covers are typically recommended. In addition, a minimum ventilation rate and electrical classification may be required by the National Fire Protection Association Code Section 820.

15.2.4 Process and Practice Modifications

Literature on the technologies that reduce emissions by minimizing the opportunity for VOCs to be volatilized from the wastewater through changes in wastewater treatment practices and processes has been reviewed and presented.[5] The findings from this literature review are summarized below.

- **Minimize the weir drops**. Weir drops can be significant sources of emissions, especially if the drop height from one liquid surface to the next is large. Some POTWs have significant drops in water surface following the final treatment process before the effluent is discharged to the receiving water surface. The liquid treatment hydraulics can, in some cases, be modified to minimize the height of weir drops and the associated turbulence that causes emissions. Covering the weir and troughs and venting the emissions to a VOC destruction system will minimize VOC emissions.
- **Minimize aeration rates**. Aerated grit chambers and aeration basins are typically the largest sources of emissions in the liquid treatment processes. Minimizing aeration rates using automatic dissolved oxygen control in the aeration basins or other methods can significantly decrease emissions. Also, replacing coarse bubble aerators with fine bubble aeration or pure oxygen will decrease emissions because significantly less air will be used. Using high purity oxygen (HPO) will result in the lowest VOC emission rates of about 1 to 15% of the influent VOCs. Trickling filters typically strip about 70 to 80% of the influent VOCs and the stripping can be reduced by force-ventilating the filter in a downward mode.[10] Replacing spray nozzles with coarse nozzles and reducing the recycle rates will minimize VOC emissions from trickling filters.

- **Avoid excessive turbulence** of influent feed system, avoid splashing at the inlet end, feed influent near the bottom of tanks and maintain a longer solids-retention time in aeration basins.
- **Reduce the number of clarifiers** needed for treatment to the minimum required. If more clarifiers are on line, then the increased surface area and detention time will result in increased emissions.
- **Use alternatives to chlorine for disinfection**. Chlorine can form certain types of chlorinated organics that can be stripped to the atmosphere in downstream weirs or drops. Alternatives to chlorine for disinfection such as UV or ozone will minimize these emissions.

Any of these and other operational changes should be closely evaluated to determine adverse impacts, if any, on the treatment process.

15.2.5 SOURCE CONTROL

Enforcement of industrial pretreatment programs primarily meant to reduce heavy metal and other pollutants that may cause damage to the sewerage system and upset downstream biological processes has also helped to reduce the inputs of VOCs to the POTWs and hence reduce their emissions. Also, ordinances controlling residential use of VOC-containing formulations reduce emissions of VOCs.[5]

It has been reported that a 94% reduction in the mass loading of perchloroethylene resulted when the East Bay Municipal Utility District (EBMUD) prohibited dry cleaning operations to discharge their processing wastes.[5] Significant reductions in VOC emissions at the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC)'s seven WRPs from 1987 through 1997 have been reported.[11] These reductions are presented in Table 15.2 and are attributed to the MWRDGC's pretreatment program.

15.3 COMPARISON OF CONTROL TECHNOLOGIES

This section provides a comparison of control technologies and includes a description of the technology, removal efficiency, potential operating problems and cross-media impacts. Technologies discussed are: thermal treatment, incinerators, flares, recuperative oxidizers, regenerative oxidizers, catalytic incineration, wet scrubbing, packed-tower scrubbers, mist scrubbers, dry chemical scrubbing, carbon adsorption and biofiltration.

15.3.1 TRADITIONAL VAPOR PHASE CONTROLS: THERMAL TREATMENT

Thermal processes are used to destroy VOCs by converting them, through combustion in an environment of excess oxygen, to fully oxidized and relatively innocuous compounds. Thermal processes also have the added benefit of being able to destroy almost all odorous compounds. The compounds formed are primarily water vapor,

TABLE 15.2
Emissions of Volatile Organic Compounds from the Water Reclamation Plants (WRPs) of the Metropolitan Water Reclamation District of Greater Chicago 1987 through 1997

	VOC Emissions from WRPs* tons/yr						
Year	Stickney	Calumet	North Side	Kirie	John E. Egan	Hanover Park	Lemont
1987	14.61	3.82	8.01	0.18	0.28	0.12	0.04
1988	26.22	8.41	6.31	0.03	0.60	0.18	0.03
1989	95.31	5.37	7.07	0.19	0.93	0.30	0.00
1990	21.86	4.79	10.27	0.05	0.20	0.11	0.00
1991	13.43	4.73	2.12	0.01	0.18	0.15	0.00
1992	11.24	2.99	2.88	0.04	0.49	0.14	0.03
1993	8.30	9.67	3.30	0.03	0.14	0.07	0.00
1994	6.56	5.36	1.82	0.02	0.14	0.11	0.02
1995	10.88	5.33	4.11	0.03	0.17	0.08	0.01
1996	7.09	5.54	1.98	0.02	0.17	0.08	0.01
1997	6.58	3.10	1.95	0.05	0.49	0.04	0.01

* BASTE model was used to estimate emissions

Source: Sajjad, A., Gluckman, M., Barney, J., Chaiken, E., Sustich, R., Tata, P. and Lue-Hing, C., Trends in reduction of toxic pollutants. Paper presented at 75th Annual Water Environment Federation Conference and Exposition, New Orleans, Louisiana, 1999.

carbon dioxide or oxidized compounds. The degree of destruction is a function of temperature, time and turbulence.

Thermal treatment systems may or may not recover heat. Systems that recover heat require less supplemental fuel. For small volumes of foul air or air streams containing sufficient heat value, heat recovery may not be cost effective, and a simple flare may be the best choice. When large volumes of foul air are treated, heat recovery is almost always cost effective. Heat recovery systems are characterized as recuperative or regenerative.

Recuperative systems recover heat continuously in a variety of ways. As an example, at Allegheny County Sanitary Authority in Pittsburgh, heat from the incinerator and afterburner exhaust is recovered through a shell-and-tube heat exchanger to provide a warm windbox for the incinerator.

Regenerative systems such as afterburners (also known as regenerative thermal oxidizers (RTOs), exchange heat in batches through ceramic media. Typically, two separate ceramic media beds are in place. Combustion exhaust gases are directed to one of the ceramic beds while inlet air (from the source to be controlled) is drawn in through the other, preheated, ceramic bed. The hot exhaust from the combustion process is directed through the cold ceramic bed side, heating the bed. While this occurs, cool combustion feed air is cycled through the hot bed side, raising its temperature near the combustion temperature. When the hot side of the ceramic media has cooled to below a set point, the inlet air and exhaust air sides are interchanged so that the heated ceramic bed preheats the incoming combustion air. Supplemental fuel gas is added in the combustion chamber to reach and maintain the desired combustion temperature, typically 1400 to 1500°F. Thermal efficiencies of regenerative afterburners may be as high as 92%.

The relatively high costs of thermal treatment due to fuel costs and the relatively low VOC concentrations found in POTW air streams make it a high-cost option for VOC control. However, thermal treatment is highly effective and reliable in control of a wide variety of different types of VOCs. The costs of thermal treatment can be more competitive if the thermal treatment hardware already exists (e.g., combustion processes such as incinerators or boilers) or the exhaust gas stream is very concentrated and has a high Btu value. Whereas other technologies may be applicable only to certain odors or VOCs, thermal systems are applicable to all. Thermal systems are clearly superior to other technologies in treating VOCs efficiently. Thermal systems can be designed with destruction efficiencies greater than 99%.

The application of thermal treatment to control VOCs and odors at WWTPs generally is limited by cost. If energy is not recovered (as when flares are used), capital costs are low, but fuel costs are high. If energy is recovered, capital costs are high, but fuel costs are reduced.

15.3.2 INCINERATORS

Biosolids incinerators may be used for VOC control under some circumstances. Fluidized bed incinerators typically are operated at sufficiently high freeboard temperatures (greater than 1400°F) and have several seconds of detention time. Under these conditions, they can be used as afterburners as well as sludge incinerators. If incinerators already exist, they can provide very cost-effective VOC control because they already require fluidizing and combustion air. Thus, the cost of treatment is only that associated with the additional drop in static pressure caused by the foul-air-collection system.

Multiple hearth furnaces are poor choices for treating VOC-laden air streams unless they are fitted with afterburners. Flashing on upper hearths creates an air stream laden with volatiles, some of which would foul heat exchange media. If an afterburner is fitted, it will burn off the problem materials and the exhaust air can be suitable for energy recovery through heat exchangers and boilers. In the process, air can be collected as the feed air for combustion and coincidental odor control is provided.

15.3.3 FLARES

Flares are vapor phase control systems that do not recover heat. Descriptions of various types of flares, design considerations and procedures and costs have been reported.[12] They are a relatively low-cost method of treating air streams containing high and variable concentrations of combustible gases. They are applicable for continuous, batch and variable flow vent gases. They are primarily used in petrochemical combusting and for burning excess digester gas at POTWs. Flares combust gases by using atmospheric air in an open flame. As such, energy cannot be recovered from them. There are two kinds of flares — ground level and elevated (laser). Ground level flares are enclosed and are not impacted by inclement weather or wind. Elevator flares are above the surrounding equipment and are used to burn large volumes of gas vented in an emergency. Temperatures of flares range from 1400 to 2500°F (760 to 1370°C). Most air streams at wastewater treatment plants contain relatively low concentrations of combustible gases, except for digester gas.

The flow rate to the flare depends on the property of the gas stream. The flame stability of the same is improved by adding flow to the waste stream by pressurizing or adding steam or air. The maximum flow through commercially available flares is about 1.06 million scfm and the minimum can be zero scfm.[13] The pollutant load to the flare to heat waste gas streams can be from 100,000 lb of hydrocarbons per flare. Flares are not as subject to stringent safety considerations as incinerators because, unlike the other confined and enclosed chamber combustion processes, i.e. incineration, they are an open combustion process. A disadvantage with flares is that the waste gas stream must have a fuel value of at least 300 Btu/scf.

A summary of the performance of flares, factors that influence their performance and other issues related to flares with respect to the control of VOC emissions of POTWs is presented in Table 15.3.[5]

TABLE 15.3
Summary of Finding on Flares for Controlling VOC Emissions for POTWs

Range of compounds	Destroy any gas waste if enough heating value >115 BTU/scf
Range of concentration	Depends on air/gas mix, wind, heating value of gas, gas velocity; not good with low BTU or dilute gases unless mixed with high BTU gases
Range of removal efficiencies	70 to 100%, with most at +90%; depends on gas BTU, gas type and wind
Known or suspect interference	Designed for average flaring event, problems with high and low BTU gas releases and windy conditions
Operational problems	Normal safety precautions, problem with elevated flares, smoke and particulates
Adaptability to POTWs	Need high BTU gas stream supplement
Level of Operations experience	Low
Number of suppliers	Low
Complexity	Complex control variables for steam injection, air/fuel mix and gas flow rate
Innovation	Low
Negative water impacts	N/A
Cross-media impacts	Steam needed for elevated flares and electricity for blowers
Energy costs	Low
Total costs	Depends on flare type

Source: Bishop, W., Witherspoon, J., Card, T., Chang, D.P.Y. and Corsi, R., Vapor Phase Control Technology Assessment, Water Pollution Control Federation Research Foundation, Virginia, 1990.

VOC destruction efficiencies of flares are typically in the 90 to 95% range. Because typical foul air streams from most wastewater treatment processes lack Btu value (less than 115 Btu/cubic ft), flares are usually a poor choice for combusting gases because of the high fuel cost. However, they can still be flared by adding supplemental fuels (acetaldehyde, acrolein, acrylic acid, acrylonitrile, cyclohexane, methanol, ethanol, formaldehyde and chloromethanes) known to be destroyed in flares. Costs of flares are influenced by the type of flare, supplemental fuel requirements and efficiency. Usually, ground level flares have higher capital costs than elevated level flares.[14] The annualized capital, and operating and maintenance costs for elevated flares are in the range of $2 to $165 per scfm (standard cubic feet per minute) per year and the overall annualized cost per ton of pollutant controlled is in the range of $14 to $6,400 per metric ton.[13]

15.3.4 RECUPERATIVE OXIDIZERS

In recuperative oxidizers, an old technology, the air stream is exposed to a flame in a specially designed combustion chamber. Figure 15.1 is a typical cross section of a recuperative oxidizer.

Recuperative oxidizers can be used on gas streams containing more than 20 ppmv of total gaseous containment. Heat from the exhaust is used to preheat the afterburner inlet. The most common recuperative oxidizing systems use shell-and-tube heat exchangers (air-to-air). Recuperative heat-recovery systems are commonly designed with thermal efficiencies of 70 to 80% for vent gas flows as large as 50,000 to 80,000 cfm. Shell-and-tube heat exchangers are commonly used in industrial

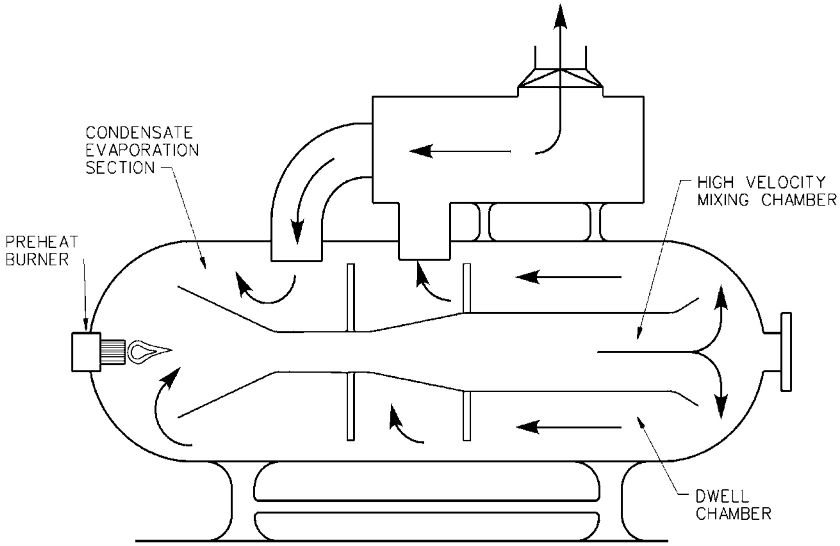


FIGURE 15.1 Schematic of recuperative oxidizer.

applications. They operate continually at relatively low pressure drops. If properly designed, they can accept a particulate loading by maintaining velocities high enough to prevent deposition of particulates and eliminate dead spots where particulates could accumulate. The materials of construction vary depending on the gases to be incinerated. Stainless steel is the most commonly used material, but Inconel steel (a nickel-chromium alloy with good oxidation resistance) is sometimes used because it resists abrasion and can withstand high temperatures. For instance, in recovering heat from a fluidized bed incinerator that contains abrasive sand and particulates, Inconel steel is a good choice.

Recuperative oxidizers normally are not sold as package units. Rather, the combustion chamber and heat exchanger are designed to suit the application and space available. Both the afterburner and heat exchanger are large. Refractory lined combustion chambers are fabricated to suit the application. Burners and heat exchangers are supplied by vendors. The cost of heat exchangers can vary widely, depending on the materials of construction and their thermal efficiency.

VOC destruction efficiencies of recuperative oxidizers depend on design criteria (e.g., temperature, residence time, inlet VOC type and concentration and degree of mixing). The temperatures required at a 1-sec detention time to achieve 99.9% destruction of some VOCs are given in Table 15.4. Typical design conditions needed to meet 98% control or a 20 ppmv effluent gas stream concentration are a combustion temperature of 1600°F, residence time of 0.75 s and proper mixing for halogenated VOC stream, a combustion temperature of 1600°F, residence time of 1 s. Use of an acid gas for cleaning the outlet gap is recommended.[15]

TABLE 15.4
Theoretical Reactor Temperatures Required for 99.99% Destruction of Some VOCs at 1-s Detention Time

Compound	Temperature, °F
Acrylonitrile	1344
Allyl chloride	1276
Benzene	1350
Chlorobenzene	1407
1,2-Dichloroethane	1368
Methyl chloride	1596
Toluene	1341
Vinyl chloride	1369

Source: U.S. EPA, Control Cost Manual, 5th ed., Ch. 3, Thermal and Catalytic Incinerators, Report EPA 453/B-96-001, 1996a.

Inlet flow rates of emissions can be in the range of 500 to 50,000 scfm. The thermal destruction of most organic compounds occurs between 1100 to 1200°F (590 to 650°C) and most incinerators are operated within the temperature range of 1800 to 2200°F (980 to 1200°C) to achieve nearly complete destruction of the VOCs.[7]

A fairly wide range of VOC concentrations can be destroyed in the recuperative incinerators. For safety considerations, the concentration of the organics in the waste gas is usually maintained at 25% of the concentration of the lower explosive limit (LEL) (U. S. EPA[15]). The best performance of these units is usually achieved at inlet VOC concentrations of 1500 to 3000 ppmv, because of the heat of combustion value of hydrocarbons that sustains combustion without the use of supplemental fuel (U.S. EPA, Undated Fact Sheet — Incinerator — Recuperative Type).

Usually, incinerators are not generally recommended for gases containing sulfur or halogenated compounds. Corrosive products such as hydrogen chloride, SO_2 and hydrogen fluoride are formed. Additional gas treatment systems may be needed for the treatment of these products. These types of incinerators are not cost effective for high-flow low-concentration gaseous streams.

The U.S. EPA estimated the costs (1995 dollars) of the recuperative incinerators processing gas streams containing inlet gas concentrations of 1500 to 3000 ppmv as follows: capital cost: \$15 to \$130 per scfm; operations and maintenance cost: \$5 to \$25 per scfm, annually; annualized cost: \$8 to \$50 per scfm, annually; overall cost effectiveness: \$100 to \$2000 per short ton, annualized cost per ton per year of pollutant controlled or removed.[16]

The efficiency of these units may be as high as 98 to 99.9%, depending on time, temperature and turbulence in the combustion chamber.[8] High combustion temperatures can cause oxides of nitrogen (NO_x) to form, which may necessitate NO_x controls because of air quality regulations. Further heat recovery can be achieved downstream of the heat exchanger with devices such as an air-to-water heat exchanger (economizer) or a waste-heat recovery boiler. However, the efficiency of heat transfer continues to decrease as the air stream becomes cooler.

Although VOC removals close to 100% are possible and recuperative oxidizers are generally more economical than normal thermal incinerators because of their heat recovery abilities, there are certain disadvantages. These are: (1) supplemental fuel costs are high, (2) they are not suited with variable flow streams and (3) they are not well suited for controlling organics containing halogens and sulfurs because of the potential for the formulation of corrosive compounds.

15.3.5 REGENERATIVE OXIDIZERS

Regenerative thermal oxidizers (RTOs) are a relatively new technology. They work best at high-flow (5000 to 50,000 cfm) and low-VOC concentrations of less than 1000 ppmv.[6,17] In RTOs, multiple beds of ceramic saddles are used to preheat the foul air stream and recover heat from the hot flue gases. In a regenerative catalytic oxidizer (RCO), a catalyst material rather than ceramic materials is used in the packed bed. RCO systems using a precious-metal-based catalyst can destroy more than 98% of the CO contained in a VOC gaseous stream; the RTOs do not reduce the CO levels. Catalysts typically used for VOC destruction include palladium and platinum. Poisoning of thick catalysts can be caused by silica, phosphorus and arsenic or other heavy metals.[16,18,19] The foul air passes through a bed of ceramic heat exchange medium of the RTOs, where it recovers a part of the thermal energy required to heat it to the incineration temperature. The gas then enters the incineration combustion chamber, which is typically maintained at a minimum of 1500°F by a gas burner. The air stream exits the combustion chamber through another bed of ceramic heat exchange medium. After a cycle of roughly 1 to 2 min, the flow is reversed and the second bed preheats the vent gas. The exhaust fan draws the clean air to the atmosphere through an exhaust manifold and valve mechanism. In the RCOs, the oxidation occurs at about 800°F due to the lower temperature used. Fuel consumption of RCOs is lower than that of RTOs.

For RTO systems, thermal efficiencies of 90 to 95% are commonly achieved and vendors routinely offer such guarantees. However, because of the low concentrations of VOCs in wastewater offgases (typically well under 500 ppm), manufacturers are reluctant to guarantee removal efficiencies. Manufacturers prefer to guarantee maximum outlet concentrations. RTOs are available in a wide range of airflows up to 80,000 cfm. They are typically not cost effective in airflow ranges less than 10,000 scfm.

Capital costs for RTOs are quite high. The capital, operating and maintenance costs are in the range of $40 to $150 per scfm and, for RCOs, the efficiency is in the range of 90 to 99%, $4 to $10 per scfm operating and maintenance, respectively. Installation costs may be high because RTOs are large and massive due to the weight of the ceramic heat exchange medium. The annualized cost ranges between $9 to $35 per scfm and the cost per metric ton per year ranges from $115 to $21,000.

The advantages of the RTOs are: (1) lower fuel requirements due to high energy recovery of 85 to 95%, (2) better destruction of VOCs due to high temperature and (3) minimal problems with chlorinated and sulfur compounds. The advantages of RCOs are: (1) lower fuel requirements due to low operating temperatures, (2) greater destruction of CO due to the catalyst used and (3) lower NO_x production.[17,20,21]

The disadvantages of RTOs include: (1) high initial cost, (2) large footprint size and weight and (3) high operating and maintenance (O&M) costs. The disadvantages of RCOs are: (1) high initial cost, (2) expensive and difficult installation, (3) greater demand for maintenance due to moving parts and catalyst monitoring, (4) possibility of catalyst poisoning, (5) need for removal of particulate matter and (6) disposal cost of spent catalyst.[16,22,23]

Because RTOs have high heat-recovery efficiencies, fuel costs are much lower for RTOs than for recuperative oxidizers. However, static pressure drops are high, typically 25 in. water gauge or more, requiring fans with high horsepower. The fans should be equipped with variable-speed drives to limit power loss caused by pressure drop swings from high to low, due to the cycling of valves. Notwithstanding these factors, savings in operation costs usually compensate for the high capital cost and, based on lifecycle cost, RTOs are the least expensive means of odor- and VOC treatment.

Particulates must be removed from the air stream before being used by the RTOs. Unremoved particulates will deposit on the ceramic medium and, under extreme circumstances, fuse on its surface. The particulate deposition will increase system pressure drops and, in severe cases, render the medium useless. In such cases, the medium must be replaced. Venturi scrubbers or a combination of low-pressure-drop cyclones are recommended upstream of RTOs for high-particulate applications (such as exhaust from biosolids dryers). Organic matter can be combusted or "baked out" by isolating the beds and subjecting them to high temperatures.

15.3.6 CATALYTIC INCINERATORS

Catalytic incinerators destroy VOCs by oxidation and use a catalyst bed of noble metals (e.g., platinum, palladium or rhodium) to promote oxidation at reduced temperatures, typically in the range of 700 to 900°F rather than the normal 1200°F used in other devices. Oxidation occurs on the surface of the catalyst. The actual steps of reaction are diffusion into catalyst pores, adsorption, oxidation, desorption and diffusion back into the air stream. Catalytic incinerators should produce less NO_x than other types of thermal treatment because of their lower combustion temperatures.

VOC destruction efficiencies can be greater than 90%, but they decrease as the catalytic material "ages" or becomes poisoned. Thermal efficiencies depend primarily on the composition of the foul air stream, uniformity of gas flow rate destruction efficiency and the type and condition of the catalyst. The temperatures required for oxidizing 80% of inlet VOCs to CO_2 are given in Table 15.5.

Typical foul-air-stream flow rates used in conjunction with packaged catalytic converters are in the range of 700 to 500,000 scfm. The waste gas is heated to 600 to 800°F by auxiliary burners before entry to the catalyst bed. The maximum design exhaust temperature of the catalyst is typically in the range of 1000 to 1250°F. As in the case of RTOs and RCOs, the pollutant loading to the units is about 25% of the LEL of the compounds combusted.

TABLE 15.5
Temperatures Required for Destroying 80% of Inlet VOCs by Oxidation to CO_2 using Cobalt Oxide and Platinum-Honeycomb as Catalysts

	Temperature, °F	
Compound	**Co_3O_4**	**Pt – Honeycomb**
Acrolein	382	294
n-Butanol	413	440
n-Propanol	460	489
Tolune	476	373
n-Butanol	517	451
1,1,1-Trichloroethane	661	7,661
Dimethyl sulfide	—	512

Source: U.S. EPA, Control Cost Manual, 5th ed., Ch. 3, Thermal and Catalytic Incinerators, Report EPA 453/B-96-001, 1996a.

Catalytic incinerators, common in industries dealing with organic compounds, are used for a variety of VOC sources and are most applicable for solvents and vent streams from hydrocarbon storage. Although sulfur compounds and chlorinated compounds are known to contaminate and poison catalytic materials, catalysts that tolerate such compounds now exist. The greatest development in this area is on catalysts that are tolerant of the oxidation of chlorine-containing VOCs. Catalysts such as chromia/alumina, cobalt oxide and copper oxide/manganese oxide have been used. Platinum based catalysts are tolerant of sulfur-containing organics, but are poisoned by chlorinated VOCs.[18–20,24,25] Because of the presence of problematic compounds in air streams at wastewater treatment plants, catalytic incinerators are usually a poor choice for thermal destruction.

Catalytic incinerators are available in a wide range of air flows and from several vendors. The capital cost of catalytic incinerators is much less than for RCOs or RTOs. The annualized capital, operations and maintenance costs are in the range of \$8 to \$50 per scfm per year. The overall cost per metric ton of the VOCs removed can be in the range of \$100 to \$5000.[18] They are smaller, less massive and easier to install than the RCOs or RTOs. Operational costs depend on the composition of the foul air stream and the catalyst. These costs are difficult to generalize other than to recognize that, for most compounds, incineration temperatures are 400 to 500°F lower in the catalytic incinerators than in noncatalytic combustors and thus may have some benefit with respect to energy costs.

Catalytic incinerators have the advantages of: (1) lower fuel requirements, (2) lower operating temperatures, (3) little or no insulation requirements, (4) reduced fire hazards and (5) less volume required. The disadvantages associated with catalytic incinerators are: (1) high initial costs, (2) possible catalyst poisoning, (3) need for particulates removal and (4) disposal of spent catalyst.[3,4,22]

Particulate matter, if present, reduces the effectiveness of the catalyst. At least one manufacturer of catalytic incinerators believes that using them to control VOCs at POTWs is not a good application of the technology. As of the mid 1990s, no installations of catalytic incinerators for controlling wastewater treatment plant emissions were known.

A summary on the performance of noncatalytic (recuperative and regenerative noncatalytic) and catalytic thermal oxidizers, factors that influence their performance and other considerations with respect to their application for controlling VOC emissions from POTWs is given in Tables 15.6 and 15.7.[5]

15.3.7 WET SCRUBBING

The distribution of a contaminant between gaseous and liquid phases is described by Henry's Law. When a gaseous contaminant initially comes into contact with a dilute liquid, an imbalance exists. This is because the natural equilibrium between the gas- and liquid-phase concentrations does not exist. As a result, there is a driving force for the contaminant to leave the gas phase and be absorbed into the liquid as the system seeks equilibrium. Wet scrubbing employs the transfer of VOC-laden gases from an air stream by absorption into a liquid medium (the scrubbing solution).

TABLE 15.6
Summary of Findings on Noncatalytic and Catalytic Thermal Oxidizers for Controlling VOC Emissions from POTWs

Factors	Noncatalytic Thermal Oxidation
Range of compounds	All compounds; less sensitive to waste gases than flares or catalysts
Range of concentration	Need higher concentrations for good destruction efficiency and high temperatures (1,000°F to 1,500°F); greater than 99% at optimum, inlet concentrations 850 to 12,200 ppmv and 1,160°F to 1,800°F; efficiency varies from 70.3% to 99.9%, with average at 94%
Range of removal efficiencies	Need higher concentrations for good destruction efficiency and high temperatures (1,000°F to 1,500°F); greater than 99% at optimum, inlet concentrations 850 to 12,200 ppmv and 1,160°F to 1,800°F; efficiency varies from 70.3% to 99.9%, with average at 94%
Known or suspect interference	Lower temperatures, not enough resident time; problems with corrosive compounds
Operational problems	Relatively reliable
Adaptability to POTWs	Requires large spaces; problems with corrosive gases and gas flow rate variations
Level of operations experience	Used for industry
Number of suppliers	Relatively high number of suppliers
Complexity	Monitoring to keep temperature and gas flow rates in optimum range
Innovation	Design has to have a heat recovery system; design NO_x control
Negative water impacts	Low
Cross media impacts	By-products of combustion — NO_x, SO_x, HC1, H_2S — if temperature drops
Energy costs	High, depends on supplemental fuel need and type of unit
Total costs	High, depends on supplemental fuel need and type of unit

Source: Bishop, W., Witherspoon, J., Card, T., Chang, D.P.Y. and Corsi, R., Vapor Phase Control Technology Assessment, Water Pollution Control Federation Research Foundation, Virginia, 1990.

The greater the exposure of a gas containing VOCs to the scrubbant and the higher the concentration of the VOCs and their driving force, the higher their absorption rate into the liquid. This driving force can, for some compounds, be increased by changing the chemistry of the scrubbant. This can be done by raising the pH of the scrubbing solution or addition of oxidants.

Wet scrubbers are designed to both maximize the exposure of the liquid scrubbant to the air stream and to maintain the chemical driving forces for getting the compounds into solution and then keeping them there. The two types of wet scrubbers most often used are packed-tower scrubbers and atomized mist scrubbers.

TABLE 15.7
Summary of Findings for Control Technologies — Catalytic Oxidation

Factor	Catalytic Oxidation
Range of compounds	Low
Range of concentration	Low concentrations, less than 25% LEL
Range of removal efficiencies	Higher temperatures (700°F to 900°F) than carbon; high for clean gas streams; lower for gases with particulates and bad compounds, such as HCl and H_2S
Known or suspect interference	Easily fouled or deactivated by POTWs gases; must raise gas temperature; some compounds suppress catalyst
Operational problems	Some explosive conditions can exist; can avoid with instruments
Adaptability to POTWs	Concerns are of large concentrations variations plus poisons and particulates
Level of operations experience	Old technology, new to POTWs
Number of suppliers	Medium number of suppliers
Complexity	Complexity is average
Innovation	Not used at POTWs; high innovation to adapt to POTWs; concentrate VOC's and reduce gas flow rate
Negative water impacts	Some liquid wastes
Cross media impacts	Produce by-products, such as HCl, CO, NO_x
Energy costs	Must preheat cold POTWs gas streams; vapor recovery systems, for a 10,000-scfm blower, costs approximately $10 to $18/scfm
Total costs	Must preheat cold POTWs' gas streams; vapor recovery systems, for a 10,000-scfm blower, costs approximately $10 to $18/scfm

Source: Bishop, W., Witherspoon, J., Card, T., Chang, D.P.Y. and Corsi, R., Vapor Phase Control Technology Assessment, Water Pollution Control Federation Research Foundation, Virginia, 1990.

15.3.8 PACKED-TOWER SCRUBBERS

Packed-tower scrubbers are the most common form of wet scrubber used for odor control in municipal wastewater plants. They represent a proven technology for H_2S-based odors.

The two general configurations of packed-tower scrubbers are countercurrent and cross-flow. Cross-flow scrubbers are considered problematic because of lower mass transfer rates and the potential for short-circuiting and dead zones. As such, cross-flow scrubbers should be considered only if space is limited or if the performance requirements for the scrubber are not high.

Countercurrent packed towers can be configured in either single or multistage arrangements. Figure 15.2 is a process flow schematic for a simple two-stage countercurrent packed-tower system. Contaminated air enters the bottom of the reaction vessel and flows upward through a bed of packing media, while contacting a downward flowing scrubbing solution. The treated air is exhausted out the top of the tower from the first stage to the second and then out through an exhaust stack.

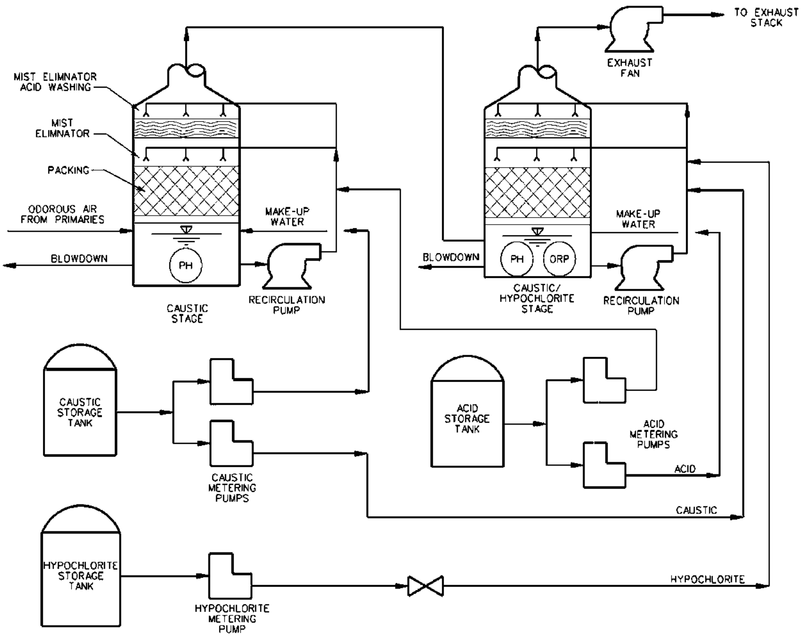


FIGURE 15.2 Simplified two-stage packed tower scrubber system.

The scrubbant chemicals enhance the ability of the solution to absorb and oxidize some contaminants. The chemicals typically used for sulfide odor removal are caustic and chlorine. However, different chemicals may be more appropriate for VOC control and the type of chemicals required will likely be dependent on the type of VOCs to be controlled.

The scrubbant solution is collected in a sump at the bottom of the tower and recirculated to the top by a recycle pump. Part of the scrubbant is continuously wasted during the process (blowdown) and replenished by a makeup solution. The blowdown removes waste products from the system. Packing media aid in scrubbing efficiency by providing a large interfacial area for contact between the contaminated air and scrubbant. A fan or series of fans placed before or after the tower move the air through the system and out the exhaust stack.

15.3.9 Mist Scrubbers

Figure 15.3 is a process flow schematic for a typical mist scrubber system. Contaminated gas enters at the top of the vessel and mixes with a fine mist. This scrubbing mist is created by atomizing a chemical solution with a pneumatic nozzle. The treated air is exhausted at the bottom of the vessel. The scrubbant is then collected in the bottom of the vessel and wasted (i.e., it is not recycled).

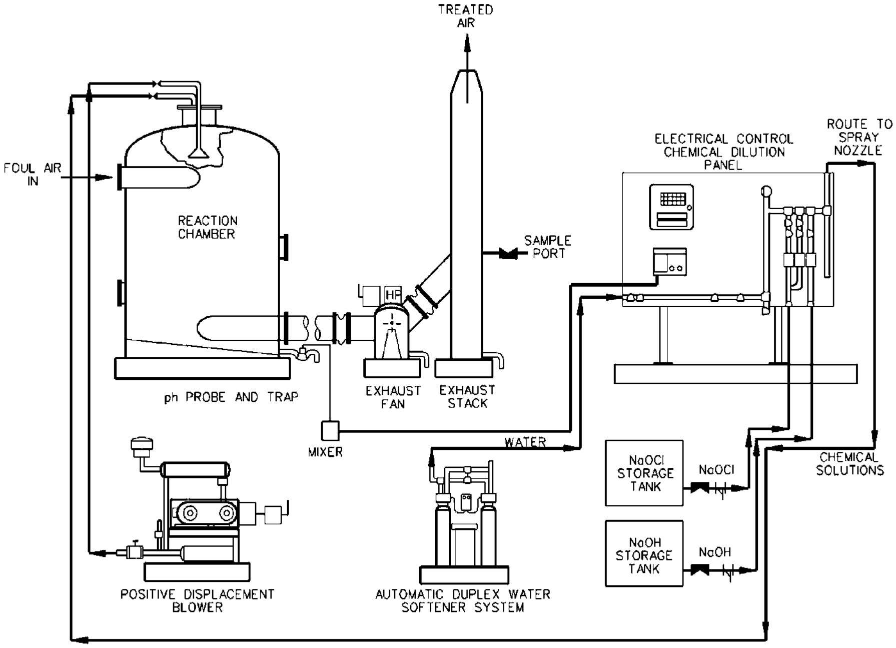


FIGURE 15.3 Mist scrubber schematic.

Some studies have found that VOC removal for mist scrubbers can be as high as 95% or more. However, other studies have shown that mist systems exhibit some removal but that the results are erratic. A mist scrubber would likely have to be pilot tested before installing a full-scale system to determine whether it would be effective for the specific application.[26,27] Mist scrubbers have the advantages of not having any packing media to foul.

Mist scrubbers have the following disadvantages: (1) spray nozzles often require periodic cleaning due to fouling and precipitate buildup unless high quality water supply used and (2) the lack of recirculation of the scrubbant solution can result in the wasting of scrubbant chemicals.

In a study funded by the Water Environment Research Foundation, a literature review was conducted on different types of scrubbers used for odor control to determine whether information was available on their efficiency to control VOC emissions from POTWs.[8] The authors also conducted pilot and full-scale studies to determine what sector influenced the control of VOC emission and how the process can be optimized for the control of VOC emissions. Based on an evaluation of the results reported from pilot-scale studies conducted at Anne Auybel County, Maryland and the Los Angeles Hyperion plant by various investigators, Wallis et al.[8] concluded that VOC removal efficiencies varied greatly among the scrubber solutions used in the single-stage packed tower scrubber. The most promising scrubber solution was a mixture of NaOH and NaOCl where NaOH primarily removed the odorous gas, H_2S, while NAOCl nonselectively oxidized the VOCs present in the odorous stream.

It is possible for secondary VOC emissions to develop due to the formation of other volatile organics under certain conditions.

Bishop et al. (1996) summarized their findings and recommendations on the use of scrubbers for VOC removal as follows:

- Packed-tower scrubbers will never effectively remove significant quantities of air toxics and ozone precursor emissions, except under very special conditions.
- Packed-tower scrubbing systems can produce toxic compounds. Nevertheless, it is possible to minimize or eliminate the production of such compounds by controlling the pH and liquid detention time, or changing the scrubbing solutions.
- POTWs should not expect any highly significant removal of VOCs from their existing wet-chemical odor-control systems without major costs for enhancements. However, a full-scale study conducted at the Washington Suburban Sanitary Commission (WSSC), a three-stage atomized mist scrubber, where the third stage contained a number of QUAD nozzles to increase droplet densities and hence the contact time, appeared to remove highly volatile VOCs.
- Although atomized mist scrubber systems theoretically have the ability to achieve significant VOC removal, they should be investigated thoroughly before they are considered acceptable and a major financial commitment is made.

15.3.10 Dry Chemical Scrubbing

Dry chemical scrubbing of VOC emissions is achieved in these units without the use of a scrubbing solution. Media such as activated carbon, activated alamina, or a combination of both can be used to achieve the removal of VOCs. Activated carbon is perhaps the most widely used for controlling odors at wastewater treatment plants, and its adsorption properties are well understood for various VOCs contained in air emissions. Activated carbon has a low adsorption capacity for most low molecular weight toxics found in POTW emissions, which are very humid. The process has had only limited success in effectively controlling HAPs in POTW emissions.[8]

15.3.11 Carbon Adsorption

Although several different types of media are used for adsorption of VOCs such as zeolites and polymers, granular activated carbon (GAC) is the most common.[28] Carbon from coal or coconut shells is thermally treated to create tiny pores. This increases the surface area and creates active bonding sites for contaminants. As contaminants fill the sites, the effectiveness of treatment decreases. Once all the sites are occupied, the carbon is spent and must be regenerated or replaced.

Carbon adsorption units are often used to remove relatively low contaminant levels in foul air streams. There are five types of carbon adsorption units:

1. Fixed rechargeable beds
2. Disposable rechargeable canisters
3. Traveling bed adsorbers
4. Fluid bed adsorbers
5. Chromate-graphite baghouses[29]

Only fixed-bed units and canisters are discussed here. This technology is usually not cost effective above a gas volume flow of 10,000 scfm. At low contaminant levels, carbon adsorbers can reduce concentrations of VOCs to very low levels. Carbon adsorption can also provide for removal of a wide range of contaminants, such as organic compounds that may not be effectively removed by standard wet scrubbers designed for H_2S removal. In a low-stage system consisting of a first-stage wet scrubber followed by a second-stage carbon adsorption, 99.7% of the total reduced sulfur compounds and 85% of the total nonmethane hydrocarbons were removed without the second-stage carbon adsorption system, the removal for the respective groups of compounds were 99.5 and 10 to 20% respectively.[29]

Traditional larger carbon adsorbing units typically have dual beds in a single vessel. One of the beds is adsorbing at all times, while the other is idled or in a desorbing mode. Odorous air enters the middle of the treatment vessel (see Figure 15.4). A fan induces flow through upper and lower media beds of activated carbon. A combination of adsorbing (gas–solid) and absorbing (gas–liquid) mass transfer lowers the contaminant concentration. After passing through the carbon beds, treated air is exhausted through a stack on top of the vessel.

Carbon media can be impregnated with chemicals such as sodium hydroxide (NaOH) to enhance contaminant removal. Once the carbon is spent, it must be regenerated or replaced. Both operations are costly and involve heavy maintenance of the equipment.

Canister units are limited to treat only low-volume and intermittent gas flows (100 ft^3/minimum, maximum) and can be thrown away when they have no adsorptive power left. However, carbon may be regenerated off site. Since VOC concentrations are not routinely monitored, chances are they are left on site even after they become useless.

Carbon scrubbers have the following advantages: (1) Typical systems may be effective for removal of low VOC concentrations for some compounds, (2) no chemical storage or metering is required (in contrast to packed-tower and mist scrubbers) and (3) they can remove a wide range of compounds that are not as effectively removed by standard wet scrubbers.

Carbon scrubbers have the following disadvantages: (1) As influent VOC concentrations increase, the life expectancy of a carbon bed decreases, resulting in high carbon replacement demands; (2) carbon bed replacement is expensive in terms of fresh carbon and the labor necessary to change beds.

It is recommended that any carbon unit be pilot tested before being installed because of the lack of experience in using carbon for VOC control. A summary of the findings on the performance of carbon adsorbers and issues relevant to POTWs is presented in Table 15.8.[5]

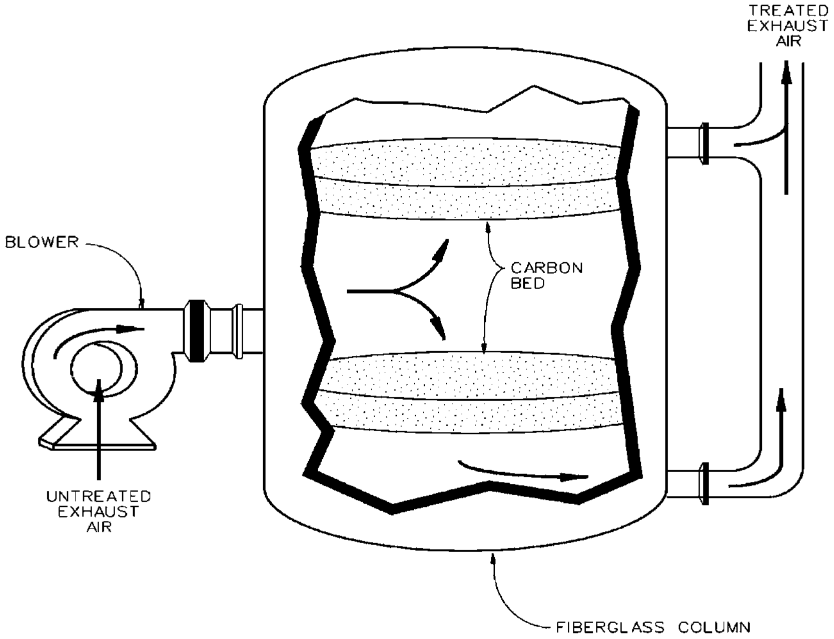


FIGURE 15.4 Schematic dual carbon bed.

15.3.12 BIOFILTRATION

Biological treatment of gaseous streams has a long history. As early as 1953, a soil system was used for the treatment of odorous air from sewer exhaust in Long Beach, California.[30] In recent years, biofiltration has become a popular choice for treating air streams containing odorous compounds. Biofiltration is also effective for treating air streams containing biodegradable VOCs. It is well established in Europe, Asia and New Zealand and is just recently becoming widely accepted as an effective odor control technology at POTWs and in industrial applications in the United States.

15.3.12.1 Process and Its Variations

Three process variations of the biofiltration technology can be used for the removal of odorous compounds such as H_2S, and VOCs such as those listed in the 1990 CAAA Title III HAPs list of compounds from waste gas streams emanating from POTWs. These are: (1) biofilters, (2) bioscrubbers and (3) trickle-bed bioreactors. Of these, biofilters are the most popular and widely used at municipal agencies. Microorganisms are immobilized or developed as attached growth on support materials or media in the case of biofilters and trickle-bed reactors. Bioscrubbers can be simply an activated sludge basin through which a waste gas stream is passed to achieve the removal of biodegradable volatile organics, or they can also contain two units, a scrubber and an activated sludge basin. Soluble waste gases and oxygen from air are continuously absorbed into water in a scrubbing tower. This water is

TABLE 15.8
Summary of Findings on Carbon Adsorption

Range of Compounds	Wide range; VOCs having molecular weights of 45–130 are well suited.
Range of Concentrations	1,000 to 10,000 ppmv. Gas flow rate: 300–100, 000 scfm; efficiency reduces with humid gas streams; for polar compounds optimal humidity is <50%; if VOC concentration is > 25% of LEL, high temperatures cause combustion of carbon bed
Removal Efficiency	High removal efficiencies possible at low concentrations with low superficial velocities and high regeneration rate
Known or Suspect Interferences	Excess capacity is needed if humidity is high in gas streams, unless gas stream is dehumidified; influent gas temperature must be less than 200°F
Operational Problems	Depends on humidity, carbon change-out and regeneration; aerosols and particulates foul carbon bed
Operational Experience	>50 years in industries; used for odor control at POTW
Complexity	Low complexity, unless breakthrough occurs or for regeneration
Innovation	Decrease relative humidity; increase retention of poorly adsorbed compounds; use alternative regeneration methods or adsorbents
Water Impacts	Process needs to be covered and ducted, entraining more VOCs in water
Cross-media Impacts	High regeneration and disposal costs
Energy costs	Costs of ducting/venting; dehumidifying, onsite regeneration, spent carbon disposal, maintenance and operations up-keep

then recycled to a biological wastewater treatment unit such as an activated sludge basin. In trickle-bed reactors, synthetic media are usually used to support the microbial growth and nutrients are supplied through a nozzle system to satisfy the growth requirements of the microorganisms. The effluent is typically recycled both for controlling pH and providing microbial reseeding. As in the case of the activated sludge scrubber system with a separate scrubber, trickle-bed reactors can also be operated in tandem with a separate scrubber, and the scrubber effluent can be fed to a trickling filter. Biofilters and bioscrubbers are the preferred systems in industry, whereas biofilters are commonly used in compost facilities and POTWs for treating odorous air. When compared with other technologies, biofilters can be more cost-effective for treating large volumes of air containing low concentrations of biodegradable organic compounds. In this section, the application of biofilters for the removal of VOCs from waste gas streams is discussed.

Two general types of biofilter configurations are available: (1) in-ground open-vessel systems and (2) modular closed systems. The modular closed-vessel systems are often pre-engineered systems employing proprietary media or system components. The selection is primarily based on the volume of air to be processed and land availability. Biofilters can also be configured into two stages, the first for removal of H_2S containing a medium such as lava rock, and the second stage containing compost.

A simplified schematic of a typical in-ground open-vessel biofilter is given in Figure 15.5. The main components of biofilters are an air distribution system, the

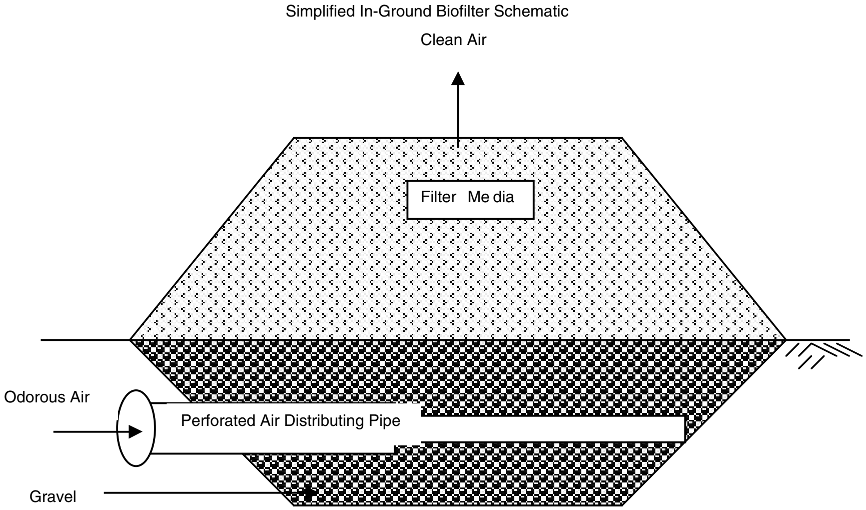

Simplified In-Ground Biofilter Schematic
Clean Air
Filter Media
Odorous Air
Perforated Air Distributing Pipe
Gravel

FIGURE 15.5 Simplified in-ground biofilter schematic.

media and a means for the control of moisture in the media and nutrients. The filter media serves four primary purposes. It provides:

1. A stable matrix through which the air stream flows evenly
2. A surface area and moist medium for sorption of compounds
3. A large surface area for microbial attachment and growth
4. Nutrients and water for sustaining the growth of microorganisms

An air stream containing contaminants passes through an air distribution system underneath the filter medium. The distribution system consists typically of a branched slotted pipe network surrounded by gravel. A filter medium is spread loosely and evenly over the air distribution system. For maintaining optimum performance, it is necessary to distribute the contaminated air throughout the bed volume. Channelization can be avoided by proper design and selection of media. Proprietary air distribution systems are available on the market and several firms also specialize in the design and installation of biofilters.

15.3.12.2 Performance: Factors and Expectations

A book on biofiltration technology and its application to control air pollution was recently published.[31] Besides discussing the theoretical and practical aspects of biofiltration, it included several case studies.

The U.S. Water Environment Research Foundation funded a study on biofiltration and released its final report,[32] in which the results of a literature survey conducted on biofilters covering the period of 1957 through 1993 are presented. Various aspects of biofilters are also discussed such as:

- Types of media and their efficacy
- Parameters that affect performance (e.g., moisture content, pH, media head loss, nutrient requirements etc.)
- Microbiological considerations
- Type of pollutants and effect of their loads on performance
- Comparison with other technologies
- Extent of application in the USA
- Mechanism and design
- Modeling
- Research needs

The removal of VOCs by biofilters depends primarily on the nature of the compound, its concentration and the removal or elimination capacity of the medium used in the biofilter. The methodology for designing and modeling biofilters has been reported previously[33] and discussed further by Devinny et al.[31]

Due to the uncertainties associated with the biodegradation of various VOCs, the elimination capacity of a medium used in a single stage biofilter is usually determined by pilot scale testing to optimize the size of full-scale biofilters for any given application. Once the single-stage efficiency is determined, a biofilter can be designed to achieve the desired efficiency. If the VOC removal efficiency of a single-stage biofilter is determined to be less than 60% for a given inlet gas stream, biofiltration may not be the best option, because it may require many stages to achieve removal efficiencies greater than 98%. This might not be cost effective.[34]

15.3.12.2.1 Media

Various media such as GAC, wood bark, loam, rice hulls, cocoa beans, soil, peat, yard waste compost (YWC), sewage sludge compost (SSC), zeollite or synthetic materials such as ceramics, perlite and plastics can be used as biofilter media. The removal of VOCs in biofilters seems to be variable and dependent on the medium used. The removal efficiencies observed for the VOCs tested and H_2S in pilot-scale biofilters with different types of media are reported in Table 15.9.[32] The media used in this study were GAC, YWC, zeolite and SSC. In most instances, all four media removed more than 99% of the H_2S and 70% of the total gaseous nonmethane organic compounds with an influent concentration of the compounds ranging from less than 10 ppbv to about 0.5 ppmv. At a detention time of 17 secs, the GAC biofilter achieved the same removal efficiency as the YWC biofilter operated at a detention time of 70 secs. Hence, the use of a GAC as a medium could result in a smaller biofilter than with the use of other media. The removal efficiency of chlorinated VOCs was found to be lower than the nonchlorinated aromatics.It was demonstrated that more than 83 and 99% of the total VOCs and H_2S present in the waste air stream of the Orange County Sanitation District were removed, respectively, by biofiltration. In contrast, the performance of a biotrickling filter manufactured by Envirogen Inc. was found to be lower, removing as little as 11% of the VOCs and 87% of the H_2S contained in the waste air stream fed to it.[35]

TABLE 15.9
Percent Removal Efficiencies of Biofilters Operated with Different Media

Compound	GAC	YWC	Zeolite	SSC
Acetaldehyde	72	84	86	82
Acetone	73	88	89	90
Benzene	74	77	52	49
CCl_4	3	8	–5	13
Chloroform	24	22	2	–20
Formaldehyde	76	77	76	76
H_2S	100	100	100	100
MEK	90	86	98	97
Methylene chloride	5	48	25	–4
MIBK	69	66	65	65
Tetrachloroethene	84	7	6	–47
TGNMO	82	81	83	79
Toluene	97	96	93	95
1,1,1-Trichloroethane	–5	26	–8	-81
Trichloroethene	64	18	27	46
Vinyl chloride	12	3	–4	–15
o-Xylene	94	93	63	95
p,m-Xylenes	95	95	64	95

Source: Torres, E. and Basrai, S.S., Evaluation of two biotechnologies — biofiltration and biotrickling filtration — for controlling air emissions from POTWs, Proc. 91st Annual Meeting and Exhibition of the Air and Waste Management Association, San Diego, California, Paper No. MP 20A 01, 1998.

GAC: Granular activated carbon

YWC: Yard waste compost

SSC: Sewage sludge compost

When compost is used as a medium, it will decompose over a period of time to small particles and tend to compact, thereby increasing the chances for the biofilter to become anaerobic due to the resistance created for air movement in the filter. Fortifying the compost with wood chips and bark will increase the life of the biofilter media. In a peat biofilter operation, it was found that the removal efficiencies for p-xylene, toluene and m-xylene were within the range of 82.1 to 95.3%, where they were significantly lower, in the range of 10.1 to 58.6%, in biofilters containing bark chips, vermiculite and Hydroballs, a synthetic medium.[36] Laboratory and field studies with compost biofilters showed excellent removals of aromatic VOCs, which averaged greater than 80%, whereas the removals of chlorinated VOCs were inconsistent and ranged between 0 to more than 60%. These low removals were attributed to the low concentrations of these compounds, which were less than 70 ppb.[37]

Some of the disadvantages of biotrickling filters and bioscrubbers in comparison with biofilters are: (1) high energy demand, (2) lower reliability and (3) poorer performance under varying loads and concentrations of pollutants. In trickle-bed biofilters, clogging of the filterbed medium can occur due to heavy microbial growths. The sloughing of the excess microbial growth can be remedied by recirculation of the effluent from the filter. However, the VOC removal efficiency of the filters may decrease till the newly formed microbial film is acclimated to the VOCs in the incoming waste stream.[38]

15.3.12.2.2 Nutrients

Biodegradable contaminants present in gaseous streams serve as food for the bacteria attached to the media used in biofilters and are metabolized to innocuous end products such as water, carbon dioxide and other inorganics. It is possible for some toxic intermediate compounds to be produced in biofilters due to the incomplete biooxidation of some organic substrates. Some types of media such as peat and compost also provide nutrients to the microorganisms. For a satisfactory and sustainable performance of biofilters, it is essential that proper nutrients, water and temperature be maintained in them. Proprietary systems have been developed for maintaining proper moisture at all times throughout the biofilter. The proper nutritional requirements to treat a certain waste air stream can be obtained by pilot tests.

15.3.12.2.3 Microorganisms

In an actively functioning biofilter, heterotrophic bacteria metabolize organic compounds. Under aerobic conditions, innocuous end products are formed without the formation of odors. Autotrophic bacteria utilize inorganic substrates; under aerobic conditions, they oxidize H_2S to sulfuric acid. If excess acid is produced, microbial activity will be hampered. Under such conditions, it may be necessary to buffer the system. Usually the required bacteria are associated with the media used, such as compost. Seeding of inorganic media is necessary to hasten the process and seeding freshly installed biofilters packed with inorganic or other synthetic organic media with activated sludge mixed liquor has been reported to be beneficial.[32]

15.3.12.2.4 Compounds

Many readily biodegradable organic compounds can be treated by biofilters. Biodegradable compounds include alcohols, ethers, aldehydes, ketones and many aromatic compounds with a single aromatic ring. Several organic amines and sulfides are also removed in biofilters. Highly biodegradable compounds can be removed to a level of 99%. H_2S removal efficiencies of close to 100% occur in biofilters. Chlorinated organics are hard to degrade in biofilters and their recalcitrance increases with the degree of chlorination.

At low concentrations of VOCs, it may not be possible to provide enough of the nutrients for the requirements of energy and synthesis of the microorganisms. This deficiency can be circumvented by providing other compounds as substrates (cometabolites). Although all biodegradable compounds can be completely removed under appropriate operating conditions, the efficiency of biofilters depends on the uniformity and magnitude of the concentration of VOCs in the inlet air and the loading rate of VOCs to the biofilters. Biofilters are not as efficient in removing VOCs as they are with H_2S.

15.3.12.2.5 Costs

Costs of biofilters have been reported for installations in the U.S., Germany and Netherlands.[39] The capital cost for enclosed systems depended on the size and degree of operational control and varied within the range of $90 to $500 per sq. ft. Operating and maintenance costs varied in the range of $0.30 to $0.60 per 100,000 scf of air processed and no media replacement cost was included. These considerably lower rates of 1990 were due to the relatively cheaper electricity costs than in other countries, where operating costs were considerably higher.

Torres et al.[32] presented cost data and an economic analysis for biofilters consisting of different media. This analysis included biofilters designed with GAC and YWC as the media in comparison with a chemical scrubbing unit. As the useful life of the medium used in a biofilter is not clearly known, the cost estimates reported were based on conservative and best-case medium life estimates. The annualized capital and operating costs for a GAC biofilter containing two independent units each treating 25,000 cfm (total of 50,000 cfm were $289,400 and $226,000, for a 5-year and 10-year media life, respectively). The corresponding annualized capital and operating costs for a YSW biofilter were estimated at $256,300 and $206,200 for 2-year and 5-year media life scenarios. Also, this study compared the estimated costs of biofilters with chemical scrubber systems. The conservative estimate of the annualized capital and operating costs for the biofilters using the GAC medium (changed every 5 years) and YWC medium (changed every 2 years), were 11 and 25% lower than for three chemical scrubbing units evaluated for processing the same air flow with one unit being kept as a back-up. For the best-case scenario, which assumed a medium life of 10 years for GAC and 5 years for YWC biofilters, their annualized costs were 42 and 56% lower than the annualized capital and operating and maintenance costs of the chemical scrubbing units, respectively.

15.3.12.3 Applicability to POTWs

For a long time, biofilters have been in use in various countries in the world for odor control. As indicated previously, their application as a vapor phase technology to remove VOCs from gas streams vented from POTWs is of recent origin and is undergoing some refinements. A recent literature review has summarized the performance of onsite biofilters with respect to VOC removals. This review also supported observations made by others, namely that, while biofilters remove odorous constituents of POTW emissions very effectively, they do not remove VOCs as effectively.[40] The percent removal efficiencies of biofilters for some VOCs reported in this review are presented in Table 15.10. The percent removals of compounds such as jet fuel; MEK; methyl isobutyl ketone (MIBK); α-pinene; gasoline vapors; styrene; toluene; xylenes; isopentane; methanol; isobutyl acetate; hexane; ethylene; ethanol/2-propanol; butanol; acetone; benzene; and benzene, toluene, ethylbenzene and xylenes (BTEX) compounds, observed by various investigators in biofilters using various types of media, were summarized and published.[31]

TABLE 15.10
VOC Removal Efficiency of Biofilters

Pollutant	Concentration, (mg/m^3)	Removal (%)	Reference
Acetone	0.03–0.09	55	Wolstenhome and Finger, 1991
	0.01	78–90	Torres et al., 1997
	0.13	78–92	Webster et al., 1997
Benzene	0.01–0.24	25	Wolstenhome and Finger, 1991
	0.03	29–78	Torres et al., 1997
	3.0	83–95	Ergas et al., 1995
	0.01	60–91	Webster et al., 1997
Toluene	0.07	82–95	Torres et al., 1997
	4.0	88–97	Ergas et al., 1995
	0.10	90–98	Webster et al., 1997
Xylenes	0.15–0.71	0	Wolstenhome and Finger, 1991
	0.4 (o-xylene)	88–91	Ergas et al., 1995
	1.1 (m,p, xylenes)	88–93	Ergas et al., 1995
	0.03 (o-xylene)	92–96	Webster et al., 1997
Chloroform	0.10–0.21	43	Wolstenhome and Finger, 1991
	0.09	0–57	Torres et al., 1997
PCE	0.02–0.51	40	Wolstenhome and Finger, 1991
	0.12	0–94	Torres et al., 1997
TCE	0.02–0.05	44	Wolstenhome and Finger, 1991

Source: Iranpour, R., Samar, P., Stenstrom, M.K., Converse, B.M., Scroeder, E.D., Cox, H.H.J. and Deshusses, M.A., Biological treatment of odor and VOCs in biofilters and biotrickling filters: survey of field experiences. Paper presented at Air and Waste Management Association Annual Conference, June 2001.

The use of GAC as a biofilter medium offers great promise for satisfactorily removing VOCs from waste gas streams of POTWs. Nevertheless, the potential impact of temporal variability of VOC concentrations on biofilter performance needs to be assessed further. Also, procedures for enhancing the biodegradation of recalcitrant organics need to be developed so that a much greater efficiency of VOC removals than hitherto have been reported can be achieved in the future. A summary of the factors related to the performance is given in Table 15.11.[5]

15.4 SUMMARY

Several technologies are potentially available to control emissions from POTWs. These technologies can be divided into five basic categories:

TABLE 15.11
Summary of Findings on Biofilters and their Performance

Range of compounds	High range of odor-causing compounds and VOC reductions; some problems with compounds that are recalcitrant
Range of concentrations	Can handle high concentrations of hydrogen sulfide and other reduced sulfur compounds; concentration range of VOCs depends on the biodegradability of theVOCs
Range of removal efficiencies	+90% for odor compounds and many VOCs; low removal efficiencies for non-biodegradable VOCs
Known or suspect interfences	Nonbiodegradable compounds or intermediate products, mass transfer limitations, temporal variations
Operational problems	Acid intermediates decrease pH that inhibit microbial activity; forms acetone; need controlled humidity and long enough residence times; nutritional deficiencies
Adaptability to POTWs	Mainly used for odor control; incidental VOC removals (high to low depending on biodegradability of VOCs) occur
Level of operational experience	Not generally used for VOCs removal, study of VOC removals mainly in research stage
Complexity	Very little if properly designed and operated
Innovation	Prehumidification of influent gases; adding limestone; enhancing biodegradation
Water impacts	Corrosion potential and entrainment of VOCs
Cross media impacts	Some problems with intermediate compounds
Energy and total costs	Medium in comparison with other technologies; costs vary depending on size

Source: Bishop, W., Witherspoon, J., Card, T., Chang, D.P.Y. and Corsi, R., Vapor Phase Control Technology Assessment, Water Pollution Control Federation Research Foundation, Virginia, 1990.

1. Traditional vapor phase controls
2. Nontraditional vapor phase controls
3. Containment
4. Process and practice modifications
5. Service control

The applicability of these technologies in controlling VOC emissions from POTWs varies. To evaluate potential effectiveness in site-specific situations, it is important to have a general understanding of how the technology works, including removal efficiency, potential operating problems, cross-media impacts and cost. This information can be used as part of the cost effectiveness evaluation required when a control technology such as BACT must be applied.

REFERENCES

1. Noll, K.C., Fundamentals of Air Quality Systems. Design of Air Pollution Control Devices, American Academy of Environmental Engineers, Annapolis, Maryland, 1999.
2. Heinsohn, R.J. and Kabel, L.R., *Sources and Control of Air Pollution,* Prentice-Hall, Upper Saddle River, New Jersey, 1999.
3. Air and Waste Management Association, *Air Pollution Control Engineering Manual*, Van Nostrand Reinhold, New York, 1992.
4. Cooper, C.D. and Alley, F.C., *Air Pollution Control: A Design Approach,* Waveland Press, Prospect Heights, Illinois, 1994.
5. Bishop, W., Witherspoon, J., Card, T., Chang, D.P.Y. and Corsi, R., Vapor Phase Control Technology Assessment, Water Pollution Control Federation Research Foundation, Alexandria, Virginia, 1990.
6. CH2M HILL, Odor Control Design Guidance Manual, Englewood, Colorado, 1999.
7. TriTAC, Guidance Document on Control Technology for VOC Air Emissions from POTWs, 1994.
8. Wallis, M., Witherspoon, J., Suzuki, S., Card, T. R., Mayer, G. and Chang, D.P.Y., *A Critical Review of Odor Control Equipment for Toxic Air Emissions Reduction,* Final Report Proj. 91-VOC-2, Water Environment Research Foundation, Alexandria, Virginia, 1996.
9. Springer, C. et al., *In-Situ* Methods to Control Emissions from Surface Impoundments and Landfills, Report EPA 600/2-85-124, 1985.
10. Card, T.R., Designing wastewater treatment plants to minimize air emissions. Presented at AIChE Summer National Meeting, Maryland, 1990.
11. Sajjad, A., Gluckman, M., Barney, J., Chaiken, E., Sustich, R., Tata, P. and Lue-Hing, C., Trends in reduction of toxic pollutants. Paper presented at 75th Annual Water Environment Federation Conference and Exposition, New Orleans, Louisiana, 1999.
12. Stone, D., Lynch, S.K., Pandullo, R.F., Evans, L.B. and Vatavuk, W.M., Ch. 7, Flares, Control Cost Manual, 5th ed., U.S. EPA OAQPS, Report EPA 453/6-96-001, 1996.
13. U.S. EPA. Air Pollution Control Technology Fact Sheet — Flares, www.epa.gov/ttn/catc/products (undated).
14. Blackburn, J.W. et al., Organic Chemical Manufacturing Vol. 4. Combustion Control Devices, EPA 450/3-80-026, 1980.
15. U.S. EPA, Air Pollution Control Technology Fact Sheet — Incinerator — Recuperative Type, www.epa.gov/ttn/catc/products (undated).
16. U.S. EPA, Control Cost Manual, 5th ed., Ch. 3, Thermal and Catalytic Incinerators, Report EPA 453/B-96-001, 1996a.
17. U.S. EPA, Air Pollution Control Technology Fact Sheet — Incinerator — Regenerative Incinerator www.epa.gov/ttn/catc/products, (Undated).
18. U.S. EPA, Air Pollution Control Technology Fact Sheet — Catalytic Incinerator, www.epa.gov/ttn/catc/products (undated).
19. U.S. EPA, Control Techniques for Volatile Organic Emissions from Stationary Sources, Report EPA 453/R-92-018, 1992.
20. U.S. EPA, Survey of Control Technologies for Low Concentration Organic Vapor Gas Streams, Report EPA 456/R-95-003, 1995.
21. Biedell, E. and Nester, J., VOCs pose a sticky situation in industry. *Pollut. Eng.,* November, 1995.
22. Gay, R., In search of the best control for volatile organics. *Environ. Technol.* May/June 1997.

23. Yewshenko, R., Hot stuff controls for emissions, *Environ. Protec.*, December 1995.
24. U.S. EPA, Fact Sheet, Thermal and Catalytic Incineration**,** (Undated).
25. U. S. EPA, Control Technologies for Hazardous Air Pollutants, Report EPA 625/6-91-014, 1991.
26. Lager, J.A., Donahue, D.W., Breen, C.A., Hunt, G.T. and Westberg. F.W., Measurement and control of volatile organic compounds and reduced sulfur species in wastewater treatment air emissions. Paper presented at Annual Water Environment Federation Conference and Exposition, Toronto, Ontario, 1991.
27. Lager, J.A., Breen, C.A., Hunt, G.T. and Laquidara, M.J., Implementation of air emissions control at the new Boston Harbor treatment facilities. Paper presented at Annual Water Environment Federation Conference and Exhibition, Miami, Florida, 1995.
28. U.S. EPA, Choosing an Adsorption System for VOCs: Carbon, Zeolite, or Polymers? Technical Bulletin EPA 456/F-99-004, 1999.
29. U.S. EPA, Control Cost Manual, 5th ed., Ch. 4, Carbon Adsorbers, EPA 453/B-96-001, 1996b.
30. Pomeroy, R.D., U.S. Patent 2, 793, 096, May, 1957
31. Devinny, J.S., Deshusses, M.A. and Webster, T.S., *Biofiltration for Air Pollution Control,* Lewis Publishers, Boca Raton, 1999.
32. Torres, E.M., Devinny, J.E., Basrai, S.S., Carlson, L.J., Gossett, R., Kogan, V., Ahn, T., Kardos, D., Shao, J., Webster, T. and Stolin, B., Biofiltration: Controlling Air Emissions Through Innovative Technology, Proj. 92-VOC-1, Water Environment Research Foundation, Alexandria, Virginia, 1997.
33. Ottengraf, S.P.P., Meesters, A.H.C., van den Oever, C.H. and Rozema, H.R., Biological elimination of volatile xenobiotic compounds in biofilters, *Bioprocess Eng.,* 1: 61, 1986.
34. Dharmavaram, S., Biofiltration, a lean emissions abatement technology. Paper presented at 84th Annual Air and Waste Management Association Meeting, Vancouver, British Columbia, Paper No. 91-103.2, 1991.
35. Torres, E. and Basrai, S.S., Evaluation of two biotechnologies — biofiltration and biotrickling filtration — for controlling air emissions from POTWs, Proc. 91st Annual Meeting and Exhibition of the Air and Waste Management Association, San Diego, California, Paper No. MP 20A 01, 1998.
36. Oh, Y.S. and Choi, S.C., *J. Microbiol,* 38: 31–35, 2000.
37. Ergas, S.J., Schroeder, E.D., Chang, D.P.Y. and Morton, R.L., Control of volatile organic compound emissions using a compost biofilter, *Water Environ. Res.*, 67: 816–821, 1995.
38. Zhu, X. Q., Alonso, C., Suidan, M.T., Cao, H.W., Kim, B. J., Kim, B.R., The effect of liquid phase on VOC removal in trickle-bed biofilters, *Water Sci. Technol.,* 38: 315–322, 1998.
39. Leson, G. and Miner, A.W., Biofiltration: an innovative air pollution control technology for VOC emissions, *J. Air Waste Manage. Assoc.*, 41: 1045–1054, 1990.
40. Iranpour, R., Samar, P., Stenstrom, M.K., Converse, B.M., Scroeder, E.D., Cox, H.H.J. and Deshusses, M.A., Biological treatment of odor and VOCs in biofilters and biotrickling filters: survey of field experiences. Paper presented at Air and Waste Management Association Annual Conference, Orlando, Florida, June 2001.

ADDITIONAL READING

1. California Air Resources Board (CARB), Suggested Control Measures for the Control of Organic Compound Emissions from Sumps Used in Oil Production in California, 1988.
2. Joffee, L.B., Use of an air-inflated dome to control VOC emissions from an aerated lagoon, *Environ. Prog.*, 9: 2, 1990.
3. Palazzolo, M.A. et al., Destruction of Chlorinated Hydrocarbons by Catalytic Oxidation, Report EPA 600/2-85-079, 1986.
4. Stone, J., Controlling VOC emissions in finishing operations, *Products Finishing,* July 1997.
5. U.S. EPA, Control Cost Manual, 5th ed., Ch. 7, Flares, Report EPA 453/B-96-001, 1996c.
6. Webster, T.S., Devinny, J.S., Torres, E.M. and Basrai, S.S., Microbial ecosystems in compost and granular activated carbon biofilters, *Biotechnol. Bioeng.*, 53: 296, 1997.
7. Wolstenhome, P.R. and Finger, R., Long-term odor and VOC performance tests on biofilters, Proc. 67th Annual Water Environment Federation Conference and Exposition, Chicago, 541–552, 1991.

16 Control Technology Evaluation

Jay Witherspoon and William Desing

CONTENTS

16.1 Introduction 349
16.2 Overview of Existing Control Technology Evaluation Processes 350
    16.2.1 Top-Down BACT Procedure 351
    16.2.2 Incremental Emission Reduction Procedure 352
16.3 Detailed Control Technology Evaluation Methodology 355
    16.3.1 Define Process Requirements 358
    16.3.2 Identify All Applicable Emission Sources (and Risks) 359
    16.3.3 Rate Potential Control Technologies 360
    16.3.4 Eliminate Infeasible Technologies 360
        16.3.4.1 Technical Feasibility Assessment 361
        16.3.4.2 Impact Assessment 361
        16.3.4.3 Determine Cost of Control 361
    16.3.5 Develop Alternatives and Rank by Effectiveness 362
    16.3.6 Evaluate Most Effective Control Alternatives 363
16.4 Incremental Emission Reduction Procedure 364
16.5 Summary 364
References 364

16.1 INTRODUCTION

Although the published MACT standards for POTWs do not impact existing facilities, emerging regulations for the control of air toxics from urban fugitive sources (e.g., POTWs) under the Urban Air Toxics Strategy and emissions from combustion sources are likely to do so. Technologies described in Chapter 15 can be applied for the control of such emissions.

This chapter presents a recommended approach for evaluating control technologies at POTWs. The material presented is extracted from the guidance document on control technology for VOC air emissions from POTWs prepared for the technical advisory committee on POTW regulatory policy issues by CH2M HILL in collaboration with the California POTWs and Air Quality Regulatory Agencies.[1] As

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

discussed in Chapter 2, the U.S. EPA's Clean Air Act air quality regulations commonly require that an analysis of emission control technologies be performed if emissions exceed certain thresholds. The most common of these evaluations are presented below. They are listed beginning with the lowest level of control and ending with the highest or most stringent control.

Both reasonably available control technology (RACT) and best available control technology (BACT) evaluations require a case-by-case determination of the control technology to be installed taking into account feasibility, availability and cost. This section describes the procedure for performing a BACT or RACT analysis. RACT is required on existing sources in areas that are not meeting national ambient air quality standards (i.e., nonattainment areas). BACT is required on major new or modified sources in clean areas (i.e., attainment areas). In nonattainment areas, technologies that achieve the lowest achievable emission rate (LAER) are required for major or modified sources. The selection of RACT and LAER technologies for any air pollution source is usually achieved by negotiations between the regulatory agency and the owner or operator of the air pollution source using the procedures similar to those applied for BACT, which are described below. While much of the discussion refers to BACT, the procedures for RACT are similar. Two other types of control technologies, lowest achieveable emission reductions (LAER) and maximum achievable control technology (MACT) generally do not require a control technology analysis. They require that controls must be used or required for other similar types of emission sources.

Air emissions from POTWs are generally characterized by low concentrations, high air volumes and multiple emission sources. Because of these characteristics, traditional control approaches are often ineffective. In many cases, it can be demonstrated that addition of emission controls will be too costly. The approach presented in this chapter recognizes the unique characteristics of POTWs and provides a consideration of traditional and nontraditional technologies. These may include various strategies such as pollutant source control (regulation of industrial and commercial discharges), enhanced liquid phase removal, wastewater process modifications and add-on control technologies.

This chapter provides an overview of existing control technology evaluation processes that includes the U.S. EPA Top-Down BACT procedure and an incremental emission (risk) reduction process. In addition, this chapter outlines a proposed approach incorporating both the Top-Down BACT and incremental emission (risk) reduction procedures and defines the evaluation and acceptance criteria used to develop the recommended control technology evaluation approach for them.

16.2 OVERVIEW OF EXISTING CONTROL TECHNOLOGY EVALUATION PROCESSES

As stated above, two types of processes are typically used to evaluate and select control technologies for a given source of emissions: the U.S. EPA top-down BACT selection process and an incremental emission reduction process. The top-down process is currently required for BACT determination by U.S. EPA. Using this process, the option with the highest level of control is selected as BACT as long as the option has no significant or adverse economic, environmental or energy impacts. Incremental emission reduction is a selection process designed to meet local air regulatory goals for reduction of air toxic pollutants, associated risk or regulated pollutant emission reduction goals as specified in local air district air quality management plans (AQMPs) or clean air plans (CAPs). The following sections provide an overview for these two control technology evaluation approaches.[1]

16.2.1 TOP-DOWN BACT PROCEDURE

The top-down process is currently used by local air districts to evaluate and determine BACT from all available and potentially applicable emission control options. The purpose of this process is to ensure the selecion of the most effective control option(s) (in terms of emission reduction potential) that has no accompanying significant energy, environmental or economic impacts. The top-down process is based on an assessment of the technical feasibility, cost effectiveness and environmental and energy impacts associated with a new or modified emission source or sources. It incorporates the following key elements:

Step 1: Identify all available control options. The first element in the top-down process is to identify all available and potentially applicable emission control technologies, i.e., technologies that have a practical potential for application to the emission sources in question. Processes that have lower emissions, product substitution, innovative technologies, pollution prevention by source control and operational changes are to be considered along with the standard add-on control devices. Although some of the control technologies identified may be eliminated later because of significant economic, energy or environmental impact, they should be included in the initial evaluation list of options.

Step 2: Eliminate technically infeasible control options. After all potential control options have been identified, a case-by-case technical feasibility evaluation is performed. The evaluation is based on a clearly documented review of the physical, chemical and engineering principles associated with the process and emission source in question. For a control option to be considered technically infeasible, it is necessary to demonstrate that specific technical difficulties that preclude the successful execution of the control option will occur. The resultant technically infeasible control options are subsequently removed from the list of potential control options to be evaluated further.

Step 3: Rank the remaining control options by control effectiveness. Each technically feasible control option is subsequently ranked according to its emission reduction potential, with the most effective control option at the top and the least effective control option at the bottom. For some cases, it is possible to rank one type of control option at various emission reduction levels depending on its specific application. A ranking hierarchy table that provides the expected emission rate, emission reduction potential and emission performance (percent reduction) is typically prepared.

Step 4: Evaluate energy, environmental and economic impacts of most effective control options. After ranking the technically feasible control options, a complete economic, environmental and energy impact analysis is performed. As part of the economic impact analysis, source- and site-specific control system design parameters are identified and detailed cost estimates are made, primarily by using equipment manufacturer cost quotations. Capital, installed and operating costs are summarized and annualized by incorporating equipment life cycles and depreciation. These cost data are compared with local air district cost effectiveness acceptance criteria or cost effectiveness data from previous control technology determinations.[2] These criteria are usually expressed in terms or dollars per ton of pollutant controlled. The cost is typically the 20-year present worth of the control system. U.S. EPA or other agencies often have a minimum cost per ton guidance that it believes should be expended on controls that will allow it to make them cost effective. This minimum cost can range from $3000 to $20,000 per ton and will vary depending upon the U.S. EPA region, the local agency and the type and size of the source. This minimum cost is typically not contained in any regulations or guidance, but is used internally by agencies to determine whether they agree with the source's assessment of the cost effectiveness portion of a BACT analysis.

In the environmental impact analysis, cross-media impacts (such as hazardous waste or wastewater generation), hazardous air contaminant impacts and visual impacts are evaluated. The energy impact analysis entails estimating direct energy consumption resulting from operating a piece of control equipment. Comparisons will also be made with other control technology determinations. The results of the economic, environmental and energy impact analyses are tabulated for each control alternative.

Step 5: Select BACT. In this final step, the results of the impact analysis are evaluated to select the BACT. The control option with the highest level of control that does not have significant or adverse economic, environmental, or energy impacts is selected as BACT.

16.2.2 INCREMENTAL EMISSION REDUCTION PROCEDURE

The incremental emission reduction procedure evaluates control technologies to achieve a specified level of emission reduction (expressed in pollutant mass or resulting risk). The procedure identifies promising control strategies and evaluates them in terms of obtaining required emission reduction goals vs. cost associated with emission controls for achieving these goals. The goal of this control technology evaluation procedure would be to identify the least-cost control option that is technically feasible and achievable in practice and that meets the required emission or risk reduction criteria of the local air district. Cost-effectiveness criteria can be calculated in terms of annualized control cost per ton of emissions reduced (as in the top-down process) or in terms of annualized control cost per level of toxicity reduced.

A risk screening analysis or a full risk assessment of the new or modified sources of emissions would be necessary to determine the risk reduction potential of possible control technologies. Local air district risk screening and assessment guidance documents should be used to conduct these analyses.

Evaluation of air emission controls may be required as part of many different regulatory requirements. The evaluation and acceptance criteria for control technologies may be quite variable depending on the nature and purpose of the regulation. To provide a comparable basis, the acceptability of technologies can be established by using the following parameters in evaluating technologies for the control of emissions:

- Total operating experience
- Predictability of performance
- Level of performance
- Known operational problems and average downtime per year
- Complexity and adaptability for retrofitting
- Commercial availability
- Secondary environmental/cross-media impacts
- Energy usage
- Costs
- Air stream concentration

A rating matrix can be developed that presents the following hierarchy of acceptability level criteria for each control technology and emission source:

- Unproven — U
- Provisional — Level 1 (L1)
- Promising — Level 2 (L2)
- Achieved in Practice — Level 3 (L3)

A description of these acceptability levels is presented in Table 16.1. The application of conventional vapor phase control technology by retrofiltering the existing process or adding a new unit process depends on the concentration of VOCs of the gaseous streams. Some technologies may be considered technically infeasible if the concentration of VOCs is below a certain level. Figure 16.1 gives applicable VOC source concentration ranges and performance efficiencies for conventional vapor phase technologies to be added on for the control of VOC emissions from a source. The level of acceptability or performance of various technologies for the control of volatile organic compounds from various unit processes of POTWs is given in Table 16.2. The user can correlate these criteria to specific provisions in the applicable regulations to establish allowable criteria for screening and acceptance of candidate technologies.[2] Engineering experience and judgment and manufacturer's information on control technology can be used to assess the potential control technologies. In addition, site- and source-specific emission and control equipment data should also be brought into the evaluation phase, if available.

Evaluating nontraditional emission controls, such as source control, by executing industrial pretreatment ordinances, introduces special considerations relative to performance monitoring and the development of enforceable permit conditions. By increasing pretreatment requirements for industries, POTW influent concentrations and associated emissions for regulated HAPs and VOCs can, in some cases, be decreased significantly.[3] Assessing the emission performance (emission reduction potential) for this type of control is not straightforward since there can be a high level of variability in discharge to the sewer. As a result, specific emission-limit permit conditions may be difficult to meet during peak periods and may also be difficult to enforce. There would also be performance-monitoring concerns relative to establishing a consistent monitoring or sampling protocol and establishing the degree of accuracy needed to assign analytical detection limits. A potential solution to these concerns would be to incorporate ranges of control technology performance into permit conditions and monitoring criteria.

16.3 DETAILED CONTROL TECHNOLOGY EVALUATION METHODOLOGY

Typical control technology selection processes have been developed for more steady state industrial emission sources than the sources encountered at POTWs.[1] The liquid source emissions at POTWs typically involve low and variable pollutant concentrations and high air volumes. For this reason, traditional vapor phase control strategies such as carbon adsorption and thermal oxidation may not be cost effective or technically feasible for emissions from POTW wastewater liquids and solids processes. For combustion processes at POTWs, a more conventional approach to technology evaluation can be used. In addition, individual wastewater processes at POTWs are fundamentally interrelated, so a change in one process will affect the others downstream. Finally, it is difficult to accurately quantify short-term excursions in liquid source emissions because of the wide variety of industries discharging to POTWs and the high variability in the concentration of pollutants discharged. For combustion processes at POTWs, a more conventional approach to technology evaluation can be used.

As a result of the unique aspects of POTW sources, an integrated approach using alternative and innovative control strategies, such as pollutant source control and process air recycle, needs to be brought into the control technology evaluation process for POTWs. These types of control strategies present a unique evaluation challenge in that the delineation between process and control technology is difficult to define and cost-effectiveness determinations are not as straightforward as traditional “add-on” controls.

The methodology suggested for use in selecting control alternatives for POTWs incorporates and refines many facets of the U.S. EPA BACT top-down and incremental emission reduction process.[4] By so doing, this methodology can be used to

TABLE 16.1
Control Technology Evaluation Criteria Matrix

Criteria	Unproven (U)	Level 1—Provisional (L1)	Level 2—Promising (L2)	Level 3—Achieved-in-Practice (L3)
Total operating experience	Limited operating experience either industry wide or POTWs	Significant experience in industries similar to POTWs	Significant experience in POTW applications	Standard practice for POTWs
Predictability of performance	Performance unpredictable	Performance somewhat predictable, but site-specific pilot testing still required	Site-specific testing not required to accurately predict performance	Highly predictable performance
Level of performance	Potentially adequate level of control	Adequate level of control	Adequate level of control	Adequate level of control
Known operational problems	Known operational problems that are potentially resolvable	Known operational problems that have a probable chance of being resolved	Operation problems have been identified and resolved	No operational problems
Complexity	Required operation skill level is not currently known	Required operation skill level is consistent with POTW industry	Required operation skill level is consistent with POTW industry	Required operation skill level is consistent with POTW industry
Commercial availability or number of suppliers	Few commercial suppliers	Single commercial supplier	Multiple suppliers	Multiple suppliers
Secondary environmental or cross-media impacts	Potentially controllable negative impact	Potentially controllable negative impact	Potentially controllable negative impact	Potentially controllable negative impact
Energy usage	Equal or less than afterburner without heat recovery	Equal or less than afterburner without heat recovery	Equal or less than afterburner without heat recovery	Equal or less than afterburner without heat recovery
Costs	Costs potentially within economic limits	Costs have been within economic limits	Costs have been within economic limits	Costs within economic limits

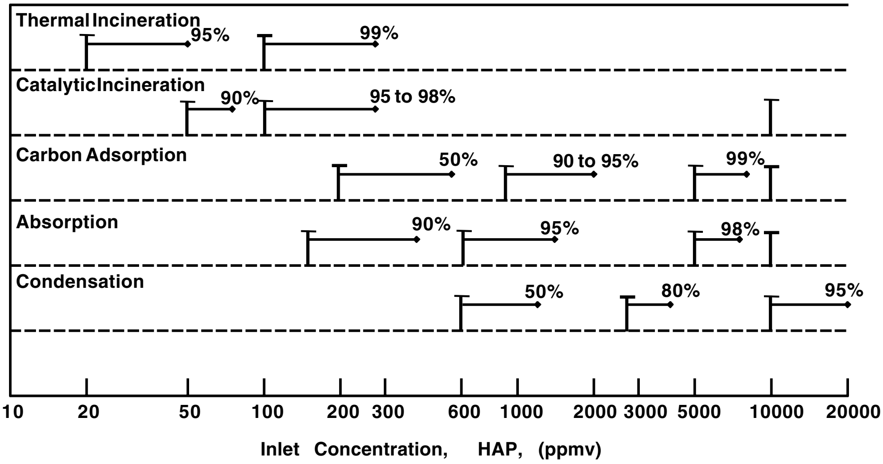


FIGURE 16.1 Approximate percent reduction ranges for add-on equipment. (U.S. EPA., Control Technologies for Hazardous Air Pollutants, EPA 625-6-91-014, 1991.)

select control measures designed to meet a wide variety of regulatory requirements, including local air district BACT requirements.

The suggested six steps for a POTW control technology evaluation methodology are:

1. Define process requirements.
2. Identify all applicable emission sources (and risks).
3. Rate potential control technologies.
4. Eliminate infeasible technologies.
5. Develop alternatives and rank by effectiveness.
6. Evaluate most effective control alternatives.

Sample worksheets are provided for guidance in the Tri-TAC Guidance Document on Control Technology for VOC Air Emissions from POTWs (TriTAC[1]). These are given in Appendices I and II. These six steps incorporate the U.S. EPA top-down BACT procedures described previously as well as the incremental emission (risk) reduction process. The following paragraphs describe each of these steps.

16.3.1 Define Process Requirements

The purpose of step 1 is to establish the appropriate regulatory framework and process requirements for selecting control technologies. At this point in the evaluation, it will be determined whether the U.S. EPA top-down analysis or an incremental emission reduction process is appropriate. If the source(s) to be controlled are new or are being modified in a way that will increase emissions (e.g., increase the plant capacity), then a BACT determination process incorporating the U.S. EPA top-down approach may be necessary. However, if the applicant is subject to a new retrofit regulation or a new regulation requiring stricter emission or risk limits, then

TABLE 16.2
Control Technology Rating Matrix

Sources	Air Stream Conc. (ppm)*	No Heat Recovery	Heat Recovery	Catalytic	Non-Ther Activated Carbon	Combined in situ Regen AC	Bio. F/S Soil Filters	Bio. F/S Process Air Rec.	En. Odor Atomized Mist	En. Odor Packed Towers	Passive	Vented Occupied	Vented Non-Occ.	Turbulence Reduction	Ops. Change	Wind-Break	Process Subs.	Ind.Pretreat	Product Subs.
Preliminary Treatment																			
Headworks	1 – 10	L1	L1	L1	L1	L1	U	U	U	U	L1	L2	L2	U	U	L1	U	U	U
Aerated Grit	1 – 10	L1	L1	L1	L1	L1	U	U	U	U	L1	L2	L2	U	U	L1	U	U	U
Primary Sedimentation	10 – 100	L1	L1	L1	L1	L1	U	U	U	U	L1	L2	L2	U	U	L1	U	U	U
Equalization	0 – 2	L1	L1	L1	L1	L1	U	U	U	U	L1	L2	L2	U	U	L1	U	U	U
Biological																			
Diffused Air	1 – 10	L1	L1	L1	L1	L1	U	U	U	U	L1	L2	L2	U	U	L1	U	U	U
Mechanically Aerated	1 – 10	L1	L1	L1	L1	L1	U	U	U	U	L1	L2	L2	U	U	L1	U	U	U
High Purity Oxygen	10 – 100	L1	L1	L1	L1	L1	U	U	U	U	L1	L2	L2	U	U	L1	U	U	U
Attached Growth	1 – 10	L1	L1	L1	L1	L1	U	U	U	U	L1	L2	L2	U	U	L1	U	U	U
Post-Biological																			
Secondary/Tertiar y Clarifiers	0 – 2	L1	L1	L1	L1	L1	U	U	U	U	L1	L2	L2	U	U	L1	U	U	U
Effluent Filtration	0 – 2	L1	L1	L1	L1	L1	U	U	U	U	L1	L2	L2	U	U	L1	U	U	U
Chlorination	0 – 2	L1	L1	L1	L1	L1	U	U	U	U	L1	L2	L2	U	U	L1	U	U	U
Solids Handling																			
Enclosed Solids Handling	1 – 10	L1	L1	L1	L1	L1	U	U	U	U	L1	N/A	N/A	U	U	L1	U	U	U
Open Solids Handling	0 – 2	L1	L1	L1	L1	L1	U	U	U	U	L1	L2	L2	U	U	L1	U	U	U
Dissolved Air Flotation	10 – 100	L1	L1	L1	L1	L1	U	U	U	U	L1	L2	L2	U	U	L1	U	U	U

Legend: N/A = Not Applicable; AC = Activated Carbon; U = Unproven; Bio. F/S = Biofilters/Scrubbers; L1 = Provisional; Process Air Rec. = Process Air Recirculation; L2 = Promising; En. Odor = Enhanced Odor Control; L3 = Achieved-in-Practice; * = VOC Concentration; Proc. Subs. = Process Substitution; Ind. Pretreat = Industrial Pretreatment; Product Subs. = Product Substitution the incremental emission reduction process would probably be more appropriate. For the latter case, selecting the highest technically feasible level of control (U.S. EPA top-down analysis) may not be needed since a lesser level of control may meet these emission or risk levels.

It may also be appropriate at this point to determine, through discussions with the air regulators, which control equipment rating criteria previously presented (unproven, provisional, etc.) would be appropriate for further evaluation. In other words, it may be determined at this stage to evaluate only provisional or higher levels of control.

At this point, the process should be defined and the regulatory setting determined. A description of the POTW processes requiring control and the overall characteristics of the POTW should be completed. Major characteristics include the level of treatment (e.g., secondary, tertiary treatment), wastewater flow rate, industrial contribution to total wastewater flow and population served. These data will help establish a means to review emission controls previously selected for comparable facilities.

Additional substeps under step 1 include:

- Determine the applicable regulations.
- Describe the definition of control technology that is acceptable (i.e., which level of control or rating levels to be evaluated).
- Establish any cost-effectiveness criteria established by the air pollution control agency.
- Identify pollutants of concern (i.e., pollutants requiring emission control).
- Define the approach chosen or required for selecting emission controls.

As described previously, many air pollution control regulatory agencies have established cost-effectiveness criteria for determining BACT. If source-specific economic impact analyses indicate that the cost-effectiveness of a given control alternative is higher than the established cost-effectiveness criteria, then this alternative may be removed from further BACT consideration. In addition, de minimis or threshold emission or risk values are often included in a BACT or emission limitation regulation. If these values are not exceeded, then the selection of control equipment may not be required.

16.3.2 Identify All Applicable Emission Sources (and Risks)

The purpose of step 2 is to completely define facility and emission source characteristics. This may also include determining baseline (uncontrolled) risks if an incremental emission (risk) reduction process is being used to select control technologies. These data will be needed to evaluate the potential control options. Worksheets 2-1 (Facility Description and Flow Sheet) and 2-2 (Emission Source Descriptions) will be used to summarize facility characteristics and identify emission sources. Worksheet 2-3 (Optional Risk Screening) may be used to calculate baseline risks and the risk reduction potential of various control technologies if needed. (See Appendix I and Appendix II.)

Under step 2 the following should be established:

- Describe each individual emission source or process including the size, number and percent of total plant influent being processed at each source.
- Determine if the emission source(s) are fugitive sources, point sources, covered or vented.
- Define and describe any existing control devices for each source and equipment identification numbers if available.
- Estimate controlled and uncontrolled emissions including a description of the method used and air stream concentration and air flow rates.
- Describe risk screening results if necessary.
- If the project risks trigger a requirement for further risk reduction, describe the risk screening methodology, list the risk impact parameters and calculate both baseline risk and, if needed, the risk reduction from the implementation of controls.

As previously described, users of this document can estimate existing (baseline) emissions from a variety of information sources, including emission factors, emission source clearinghouse data for comparable sources (from U.S. EPA, state air agency, or local air district), or site-specific emission test and sampling data. In addition, local air district risk assessment guidance documents such as the California Air Pollution Control Officers Association (CAPCOA)[5] are available to assist the user in conducting risk screening analyses.

16.3.3 RATE POTENTIAL CONTROL TECHNOLOGIES

The purpose of step 3 is to conduct a preliminary evaluation and rate all potentially applicable control technologies according to the criteria discussed previously. Potentially feasible control technologies should be identified and rated as a first step in the feasibility evaluation. An evaluation criteria code (e.g., unproven, provisional, promising or achieved in practice) should be assigned to each potential control technology for each source of emissions. Depending on the control technology acceptance criteria defined during step I of the overall process, it may be appropriate at this stage to eliminate certain control measures from further analysis because of their limited POTW application or unpredictable performance. However, it should be stated that the purpose of this step is not to screen control technologies but to establish the groundwork for the formal feasibility evaluation (step 4). If additional site-specific data that suggest potential exclusion or inclusion of a given control technology are available, then the data should be brought into the process at this stage.

16.3.4 ELIMINATE INFEASIBLE TECHNOLOGIES

The purpose of step 4 is to conduct a feasibility evaluation for each of the remaining control technologies. The evaluation will be based on a technical feasibility assessment (comparable to the U.S. EPA top-down BACT procedure) as well as a generalized economic, environmental and energy impact assessment. Infeasible controls will be eliminated during step 4.

16.3.4.1 Technical Feasibility Assessment

The feasibility evaluation is based on a review of the physical, chemical and engineering principles associated with each control technology and potential emission source application. To eliminate a control technology because of its technical infeasibility, it would be important to demonstrate that specific technical difficulties will occur that will prevent successful execution of the control technology. To determine the technical feasibility of each control technology, qualitative information on the applicability, status of current knowledge and typical performance associated with the applicable control technologies should be established. Additional technical performance input from manufacturers or technical publications should also be used to effectively assess the technical feasibility of the applicable control technologies.

16.3.4.2 Impact Assessment

During this sub-step, it may also be appropriate to eliminate control technologies that have potential adverse economic, environmental or energy impacts. A qualitative assessment of the energy and environmental impacts associated with each potentially applicable control technology should be done at this point. This assessment will provide a preliminary indication if an adverse or significant energy or environmental impact is possible with some of the candidate technologies assessed. Additional technical information from manufacturers or technical publications should be used in assessing the energy and environmental impacts.

16.3.4.3 Determine Cost of Control

Under this sub-step, the cost of implementing each control technology not yet eliminated should be determined. To conduct a detailed cost analysis, it is recommended that the procedures outlined in the U.S. EPA Office of Air Quality Planning and Standards (OAQPS) Control Cost Manual be used.[6] This document recommends the use of site-, source- and vendor-specific cost data (if available) in place of the cost factors used in the generalized approach. The U.S. EPA control cost manual does, however, include cost factors if needed. These costs should include the following:

- Total capital cost of all equipment and appurtenances
- Annualized operating and maintenance costs including power, labor, chemicals, fuel and preventive maintenance costs
- Annualized capital cost
- Total annualized cost of control

Calculations can be based on the procedures summarized in another U.S. EPA document identifying control technologies for hazardous air pollutants.[7] The cost approach taken in the document is somewhat less detailed than the approach recommended for a detailed BACT cost analysis; however, it enables the user to obtain a general indication of design and cost parameters without incorporating more complex calculations.

Using the total annualized cost, the overall cost effectiveness of a given control technology should be calculated. Cost effectiveness can be defined as the total annualized control cost divided by the tons of emissions reduced. Alternative expressions of cost effectiveness include total annualized cost divided by the level of toxicity or risk reduced. If the calculated cost effectiveness using these generalized data clearly exceeds the defined cost effectiveness criteria for a given application, then the control technology may be eliminated from further consideration. If the calculated cost effectiveness is well below the defined criteria, then it may not be necessary to perform a detailed cost impact analysis. A detailed (i.e., a site- and manufacturer-specific) cost impact analysis would be needed if the calculated cost effectiveness is close to the defined criteria.

Control technology options that survive the screening process done in steps 1 through 4 (or those still marginally considered reasonable) should be generally carried forward into the control alternative development and detailed analysis steps of the process (steps 5 and 6).

16.3.5 Develop Alternatives and Rank by Effectiveness

After completing the feasibility evaluation (step 4), the most infeasible control technologies are eliminated from the analysis. During step 5, control alternatives can be developed from the remaining potentially feasible control technologies. A control alternative can be for one emission source, a group of sources, or for the facility as a whole. Effective integration of multiple control technologies to a given control alternative is necessary since altering one emission source at POTWs will, in many cases, affect other upstream and downstream sources of emissions.

The generalized emission performance and impact data associated with each control alternative should be summarized. Any regulatory acceptance criteria (e.g., required emission reductions, risk levels, new emission standards) should also be identified.

If the top-down BACT analysis is required, then each control alternative should be ranked by overall control effectiveness with the highest emission reduction potential. This ranking hierarchy will constitute the starting point for the detailed control alternative analysis phase of the evaluation (step 6).

If the incremental emission reduction process is used to select the control technologies, then it is suggested that each control alternative be ranked according to cost effectiveness. If appropriate regulatory acceptance criteria are met, then the most cost-effective alternative can be selected and no further analysis is needed. If it is still not clear which control alternative should be selected, then the detailed alternative analysis phase would be needed.

If the regulatory acceptance criteria are based on risk, it may be appropriate during this phase to conduct a screening-level risk evaluation to compare project risks with acceptance risk criteria. A more detailed risk assessment can be performed during the detailed impact analysis (step 6 in overall evaluation process).

16.3.6 EVALUATE MOST EFFECTIVE CONTROL ALTERNATIVES

The last step of the control technology evaluation process entails a detailed site- and source-specific economic, environmental and energy impact analysis for each of the control alternatives developed.

During the detailed economic impact analysis, source- and site-specific control system design parameters are identified and cost estimates made. Control equipment cost data are typically provided by the equipment manufacturer, with additional cost data obtained through control technique guideline documents or from trade publications. It is important to distinguish between basic emission-related equipment and the emission control system. Establishing these "battery limits" allows for a common ground of comparison between control technologies and alternatives.

Capital, installed and operating costs are summarized and annualized by incorporating equipment life cycles and depreciation. Control costs are estimated in terms of total annualized cost (control cost per year), average cost effectiveness (total annualized control cost per ton of emission reduced from the baseline or uncontrolled emission level) and, in some cases, incremental cost effectiveness (difference in annualized cost between two control alternatives divided by the corresponding difference in tons of emissions reduced).

In addition, if the regulatory acceptance criteria for a given project are based on reducing the overall project risk, then cost effectiveness may be more appropriately estimated in terms of annualized cost of control per level of toxicity or risk reduced. These cost data are compared with local air district cost effectiveness acceptance criteria or cost effectiveness data from previous control technology determinations (e.g., BACT Clearinghouse data).

In the environmental impact analysis, control option impacts such as solid or hazardous waste generation, discharge of generated wastewater, visibility impacts due to the control option, or the generation of unregulated or hazardous air contaminants are evaluated. (If the regulatory acceptance criteria are risk-based, then a risk assessment may be performed as part of the environmental impact analysis.)

The energy impact analysis entails estimating direct energy consumption resulting from operating a piece of control equipment. As an example, a thermal oxidizer used to combust VOCs would in all likelihood have supplemental fuel consumption requirements. The impact analysis would require estimating the fuel consumption cost per ton of emissions reduced in the thermal oxidizer. Comparisons would also be made with other control technology determinations to assess if the energy impact is excessive.

As with the generalized control alternative comparison, each alternative should be ranked according to control effectiveness if a top-down BACT process is required, or ranked according to cost effectiveness if the incremental emission reduction process is used. The control alternative with the highest level of control (highest emission reduction potential) that does not have any significant or adverse impacts will be selected if the top-down BACT process is required. The least costly control alternative that meets the regulatory acceptance criteria and also does not have any significant or adverse impacts will be selected if the incremental emission reduction process is used.

An example of the top-down BACT evaluation methodology is reproduced in Appendix I along with blank worksheets from the Tri-TAC document.[1]

16.4 INCREMENTAL EMISSION REDUCTION PROCEDURE

To achieve a specified level of VOCs or HAPs emissions (expressed as pollutant mass to be removed or resulting risk), the incremental reduction procedure[1] can be applied. This procedure would identify technologies that offer promise and evaluate them for emission reduction goals and costs associated with such goals. The ultimate goal of this procedure would be to identify the least cost control option that would be practical and technically achievable for the emission and risk reductions required by the local regulatory agency. Costs associated with the technologies identified for analysis can be calculated in terms of annualized cost per ton of emission reduced or level of toxicity reduced as in the top-down BACT procedure.

A risk screening analysis or a full risk assessment of the new or modified sources of emissions would be necessary to determine the risk reduction potential of candidate technologies. Risk screening and assessment guidance provided by agencies such as the local regulatory bodies or CAPCOA[5] should be used to conduct these analyses.

An example of the incremental emission or risk reduction procedure along with a blank sheet on optional risk screening, which is required in addition to the blank sheets required for the top-down BACT procedure (included in Appendix I), is reproduced from the TriTAC document and included in Appendix II.

16.5 SUMMARY

Traditional air emission control approaches are often ineffective at POTWs, where air emissions are generally characterized by low concentrations, high volumes and multiple sources. In recognition of the unique characteristics of POTWs, it may be useful to consider a control technology evaluation approach that incorporates two concepts: the U.S. EPA top-down BACT procedure and the incremental emission (risk reduction) procedure. The suggested methodology, comprising six sequential steps, can be used to select control measures designed to meet a wide variety of requirements, including local air district BACT requirements.

REFERENCES

1. Tri-TAC, Guidance Document on Control Technology for VOC Air Emissions from POTWs. Jointly sponsored by League of California Cities, California Association of Sanitation Agencies and California Water Pollution Control Association, California, 1994.
2. U.S. EPA, RACT/BACT/LAER (Clearing House Data), www.epa.gov/ttn/catc/rblc (updated quarterly), 2001.

3. Water Environment Federation, Hazardous Waste Management at Wastewater Treatment Plants, Alexandria, Virginia, 1994.
4. U.S. EPA, *RACT/BACT/LAER* Clearing House: A Compilation of Control Technology Determinations, Fourth Supplement to 1990 Edition, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, June 1994.
5. California Air Pollution Control Officers Association (CAPCOA), Air Toxics Risk Assessment Manual, Cameron Park, California, 1989.
6. U.S. EPA, EPA Air Pollution Control Cost Manual, 6th ed., EPA-452-02-001, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, 2002.
7. U.S. EPA. Control Technologies for Hazardous Air Pollutants, EPA 625-6-91-014, 1991.

17 Epilog

Jay Witherspoon, Prakasam Tata and Cecil Lue-Hing

CONTENTS

17.1 Introduction 368
17.2 Major Factors Affecting VOC Emissions 369
  17.2.1 Site-Specific Considerations 369
  17.2.2 Relationship to Odor Control 370
17.3 Roadmap Approach to VOC Emissions Control 371
  17.3.1 Purpose of the Roadmap 371
  17.3.2 The Roadmap Concept 371
  17.3.3 Roadmap Approach 372
    17.3.3.1 Program Internal Audit 372
    17.3.3.2 Benchmarking 373
    17.3.3.3 Resource Estimates for a Fully Implemented Air Quality Compliance Program 373
    17.3.4 Benefits of a Proactive Approach 373
17.4 Roadmap Major Air Quality Control Program Elements 374
  17.4.1 Process Monitoring and Control 374
  17.4.2 Recordkeeping and Reporting 375
  17.4.3 Preventive and Corrective Maintenance 375
  17.4.4 Regulatory Interactions and Odor Complaint Response 375
  17.4.5 Compliance Investigation and Follow-Up 375
  17.4.6 Process Optimization 375
  17.4.7 Research, Special Studies, Troubleshooting and Emissions Characterization 376
  17.4.8 Planning, Design, and Construction 376
  17.4.9 Administrative Activities 376
  17.4.10 Determining General FTE Requirements 376
  17.4.11 Correlating Best Management Practices 377
17.5 Air Quality Compliance Program Case Study 377
  17.5.1 Establish Responsibilities for Air Quality Assessment, Prevention, Response and Control 385
  17.5.2 Give Priority to a Focused District Wide Air Quality Assessment, Prevention, Response and Control Program That Matches Routine Good-Neighbor Actions 385

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

17.5.3 Continue Supporting POTW ECHO as a Leader in Air Quality Assessment, Prevention, Responses and Controls 386
17.5.4 Use Incident Command System to Respond to Air Quality Permit Violation or Breakdown Event 387
17.6 Implementing the Roadmap at POTWs of Any Size 387
17.7 Summary 390

17.1 INTRODUCTION

The focus of the preceding chapters of this book is on VOC emissions and their control from POTWs, which is one of the important aspects of air quality compliance. However, as pointed out in Chapter 1, air quality issues also encompass emissions of odors and criteria pollutants. In this chapter, the term air quality is used to describe VOC emissions control as well as in the larger sense. This chapter will provide tools, concepts, policies and information for POTW managers to develop or optimize air quality compliance activities and air permitting needs and provide a few tools to assess labor and capital needs to maintain an air quality compliance program's long-term viability.

Optimization of this information will rely on specific steps to assess POTW needs and current practices, standards and resources, and to evaluate them with those of other utilities. As an example, tools provided to assess labor and capital needs to maintain an air quality program are focused on POTWs less than 50 mgd, as many U.S. POTWs fall at or below this flow rate. However, using scaling factors and other techniques, managers can develop an approach that makes sense and is in line to adequately staff the various compliance, operations, maintenance, engineering and administration tasks seen for POTWs with smaller or larger flows.

This effort is not a comparison of air compliance needs at various wastewater treatment plants, but a comprehensive look at what is needed for a POTW to develop, maintain or build upon its current air quality compliance and control program based on successful programs at other plants. The result is a detailed program or "critical mass" approach that includes program elements, air emissions inventory information, measurement techniques and viable control options required to properly manage a good, complete program.

This chapter provides insights and recommendations for POTWs to implement a fully functional air quality and compliance program. First, major factors affecting VOC emissions are summarized from preceding chapters. Then, a roadmap approach to VOC emissions control is presented. A critical mass approach or program ties all the chapters together into a complete air quality compliance program. Nine major air quality control program elements are described and then evaluated by tasks and functional organizational units for POTWs less than 50 mgd. BMPs for air quality compliance per program element for POTWs of this size are then discussed, followed by a case study. The last section in this chapter describes how "rules of thumb" developed for POTWs less than 50 mgd can be scaled up or scaled down to apply to plants as small as 1 mgd or as large as 1 billion gallons per day.

17.2 MAJOR FACTORS AFFECTING VOC EMISSIONS

Since focusing on VOC emissions control in the mid 1980s, POTWs have made great strides in learning more about the sources of VOCs, ways to characterize VOC emissions and strategies to control them. For example, major studies conducted 10 years apart have demonstrated a significant reduction in the VOC load of POTW influents, which is attributable to diligent efforts of municipal agencies to enforce pretreatment programs to reduce toxics loads to POTWs. It also has been shown that daily, weekly and seasonal variables in VOC concentrations do occur. Other "lessons learned" include the determination that very few compounds are of general concern for air toxic emissions from liquid processes at POTWs, that emissions of VOCs from the dewatering processes are small, especially when compared with emissions from the other wastewater treatment processes, and that VOCs can be formed in unit processes such as chlorination although the influent to such unit processes may have negligible VOCs.

However, information gaps still exist. Research, or in some cases the lack of it, has shown that a great deal more study needs to be conducted to clearly understand and validate the nature and magnitude of emissions from sewers. Another concern is the variability in the occurrence of various VOCs, their concentrations at various treatment plants and significant differences in their concentrations. This makes it difficult to accurately predict the VOC loadings to treatment plants and, hence, their emissions. Major municipalities should consider regular (e.g., monthly) monitoring of influent VOC concentrations to ensure that VOC loadings to their treatment facilities are under control.

One of the most significant facts to emerge is the site-specific nature of VOC emissions. This section describes site-specific factors and also explores the link between VOC emissions control and odor control.

17.2.1 SITE-SPECIFIC CONSIDERATIONS

Site-specific considerations are important in developing effective VOC emission-control strategies. Unlike odors, which are intrinsic to treatment plants, VOC emissions are primarily caused by external inputs imposed on the system. These include:

- **Degree of industrial waste discharged to the system**. Many VOCs are used in various industrial manufacturing and process applications, and industrial discharges are by far the most important single factor in determining the extent of VOCs in the system. Some studies have indicated that up to 98% of VOCs to a system are attributable to industries. Chemicals most commonly contributed by industries are benzene, methylene chloride, trichloroethylene, xylenes and carbon tetrachloride. Industries associated with these and other chemicals include metal finishing, synthetic organic chemical manufacturing, textiles, petrochemicals, petroleum refining, plastics, semiconductors, glass manufacturing, pharmaceuticals, dyes, synthetic rubber, paint and pigment, electroplating, pesticides, degreasing operations, explosives and natural and synthetic resins.

- **Type of collection system**. Of the three types of collection systems — sanitary, stormwater and combined — the combined sewer systems seem to contribute more VOCs. Runoff from combined sewer area overflows, particularly in heavily urbanized areas, has been reported to contain a higher concentration of VOCs than from systems having separate sewers. The measured gasoline component VOC inputs to treatment facilities with combined sewers are proportional to the combined sewer areas, suggesting that the possible source of these VOCs is nonpoint runoff to combined sewers.
- **Location**. Everything being equal, facilities located in hot climates will tend to have more VOCs than those located in colder climates.
- **Unit processes**. Certain processes will generate more VOCs than others.
- **Size**. System size is important in evaluating VOC emissions control strategies. For comparable-size POTWs, one serving urban areas where industries are located and their wastes are tributary to the POTWs, and one where there are no industries, it is natural to expect lower emissions from the POTW that receives a nominal amount of VOCs from domestic and commercial sources and no VOCs from industries. Hence, the size of the plant where VOC emissions control would be needed is a function of the VOC loading to the plant and its ability to attain a "major source" status. In contrast, odor generation potential of a treatment plant is dependent to some extent on its size but, more importantly, on how it is operated and maintained.

Thus, in order to keep a well-operated and -maintained treatment plant that satisfies all the air quality compliance requirements, in terms of both VOC and odor control, a certain minimum amount of effort in terms of allocation of human and material resources (or "critical mass") should be made. The "critical mass" required varies from plant to plant and depends on several factors, including the size of the plant, location, regulatory requirements, proximity to residential communities, industrial discharges, etc. These factors and the roadmap concept are further discussed below to arrive at the critical mass required by a given treatment plant.

17.2.2 RELATIONSHIP TO ODOR CONTROL

The focus of this book is not an odor control or assessment program, but the overall air quality component of the program. However, the control of VOC emissions and odors is related, although not directly comparable. As mentioned above, VOCs are generally contributed by external impacts on the system, in contrast to odors, which are intrinsic to POTWs treating sewage. However, VOC control measures frequently have collateral odor-control benefits, and the reverse is also true. Many odor control measures have a collateral benefit in reducing VOC emissions. POTW managers need to target cost-effective technologies to solve both problems. The roadmap approach presented below is one tool in the manager's arsenal to help accomplish this objective.

17.3 ROADMAP APPROACH TO VOC EMISSIONS CONTROL

This section describes how to develop a roadmap to a fully compliant air quality program pulling from and using all the strategies and approaches presented in previous chapters.

17.3.1 Purpose of the Roadmap

This roadmap is to be used by readers to evaluate their own air quality compliance programs. This evaluation can then be used to expand or make changes to existing programs, develop new programs, or inform management to what degree existing programs are in compliance and what activities may be needed to avoid air quality-related fines and violations. Because even the "best" air quality compliance programs require some fine tuning and adjustments, readers are encouraged to use this roadmap approach to assess, plan, develop and implement successful, fully compliant programs, as well as to enter into meaningful focused discussions with internal program funders on what is needed or not needed to have a fully compliant program. When such a roadmap is in place, POTW managers can also use it in their outreach activities to convince the public that management is responsive to their concerns and needs.

17.3.2 The Roadmap Concept

POTWs will continue to face many challenges in complying with all federal, state and local air quality regulations and laws. As POTW-wide air quality policy, regulatory requirements associated with air emissions and community liabilities continue to expand, POTWs need to develop a focused approach or roadmap to identify developing air quality issues, assess current control and compliance needs, prevent possible onsite and offsite air emissions impacts, respond to both internal and external air quality regulatory agency requests and control current and future air emissions.

Many parts of a comprehensive roadmap may already be present at a POTW, but it may not be completely guided by management or fully implemented or integrated into the organization because of unclear roles and responsibilities, or may be due to insufficient ability to handle today's air emissions assessment and control requirements. For purposes of this chapter, the roadmap is a conceptual program or a "critical mass program" that is currently not defined or developed at most POTWs and, as such, will be laid out here to assist POTWs in defining fully functional air emissions assessment, permitting, prevention, response and control programs. Many current air emissions assessment and control programs are very strong, particularly in areas classified as severe or extremely severe nonattainment areas. Thus, to implement this roadmap, only minor changes and new program elements may be needed.

To use this roadmap, each POTW will need to evaluate its current resources and practices quickly, while focusing on assessing the functional organization and then evaluating and recommending improvements. The basis for this assessment is a conversion of the POTW's dedicated or part time air quality-related compliance staff into full-time equivalents (FTEs) performing diverse functions in various departments such as operations, engineering, design, construction, inspection, maintenance, public outreach, source control, repair and replacement staffs. Communication and decision practices, standards and resources need to be identified for the plants and collection system under three approaches — current levels, future levels using current level approaches and future need levels based on BMPs used by peer agencies.

At most POTWs, air quality compliance assessment, permitting, prevention, response and control staff are located in several divisions or departments that are part of both corporate and operating units. The "roadmap" corporate responsibilities include handling POTW-wide responsibilities for tracking air quality compliance and control activities; responding to air quality regulatory agencies and the public; procuring and handling the chemicals needed for air quality control; providing system-wide air quality emissions control guidance; performing air quality measurements and sampling; conducting system-wide research; providing system wide process engineering; conducting system-wide support functions, including facility construction and engineering; maintaining community contacts; and outreach activities. Roadmap operating units are defined as the departments, divisions or groups that operate or maintain specific air emissions control measures or equipment.

17.3.3 ROADMAP APPROACH

The roadmap approach typically includes performing an internal audit of the existing program, benchmarking against peer agencies, identifying the components of a solid roadmap and providing resource estimates to implement a fully compliant air quality program at the POTW. The approach is summarized below.

17.3.3.1 Program Internal Audit

The POTW's internal audit program can be accomplished in three phases: processes and practices review, staff interviews and site visits. To learn and identify the strengths and weaknesses of the POTW's current air quality compliance program, personnel to target for interviews should be from different divisions and departments. This group should include both corporate and operating units' staff such as operators, maintenance staff, supervisors and managers at all levels who have any air quality-related role or responsibilities.

The audit serves as a vehicle for operating units to express their concerns or praises on how well the air quality program had been interacting with them. It should be noted that some air quality permits can take over 90 days to several years to attain, which can leave operations without that new process or equipment needed during the permitting period. Audit results should be presented to the staff interviewed and operating units set up without "naming names and finger pointing" to ensure honest and direct responses without fear of censure directed at the interviewed person. These audit results should be presented in summary format, focused only on the air quality compliance program and not on individuals, to show trends or indicators of service provided and how all operating and corporate units receive it.

17.3.3.2 Benchmarking

Many peer POTW wastewater districts or cities are available to compare their air quality compliance programs against a POTW's program. Each responding peer agency should provided information on the number and types of air emissions control equipment and approaches; number of and type of air quality permits; number of past air quality violations, if any; number of air emissions control facilities; number of air quality-related staff at both corporate and operating unit levels; program elements; and air quality compliance program organization. Agencies selected for comparison should be a mix of large and small POTWs both inside and outside a POTW's service area and state.

17.3.3.3 Resource Estimates for a Fully Implemented Air Quality Compliance Program

Based on the results of the three-phased audit and benchmarking, a POTW will be able to identify elements of a fully implemented air quality compliance program. This effort includes suggesting basic program elements and providing resource estimates for implementation.

17.3.4 BENEFITS OF A PROACTIVE APPROACH

Most successful, compliant air quality programs include clear understanding of roles and responsibilities among the various functional groups inside the POTW needed for successful program implementation. Such groups include the engineer, operator, mechanic, administrator, program funder, program auditor, air quality permitting staff, regulatory agency contact and air quality laboratory and support staff.

Many U.S. POTWs have dedicated FTEs to manage and implement their existing air quality compliance, monitoring and control programs at their plants and in the collection system. These programs, besides VOC control, also often include managing odor impacts and control needs. These programs can significantly vary from state to state in detail, focus, and total POTW's implementation costs. Typically, states like California, New Jersey and New York require fairly comprehensive air quality compliance programs compared with other states, but all states are required to be in compliance with the CAAA of 1990.

This analysis also indicates that several POTWs use a proactive approach vs. a reactive approach to address air quality compliance. In fact, these POTWs seem to see significant cost benefits to a proactive program. These benefits include (1) reductions in potential exceedance events, violations, fines, air quality permitting delays and equipment down time, (2) compliance documentation, (3) identification of staffing needs and compliance costs, (4) good recordkeeping and (5) several other noncost-related benefits including meeting the POTW's good neighbor or compliance charters or policies, knowledge of their air emissions and compliance status and ability to factor air quality needs into any plant expansion, modification or addition — right from planning stages through start-up to grave.

Usually, the reactive approach finds a POTW unprepared for a surprise air quality regulatory agency permits inspection, an upset or breakdown event, or an offsite impact odor event, and much time and significant effort are expended during the course of such events. A proactive approach evaluates how to manage or control the situation before it can happen and then address the event quickly when it does occur without needing significant time to set up and investigate the event. The latter can be a call to arms for many plants that might have been ignoring the inspections, compliance issues, lack of permits, odor complaints, etc. and hoping that they would just go away until the next event. However, one problem of "wishing away" these events is that it may cost more in control equipment, public relations efforts, permit conditions and costs, and staff labor needed to handle the situation vs. proactively addressing the event (one at a time) and working to show compliance on a continuous basis. Under either approach, the air quality regulatory agency and public will have the final say on whether the plant has successfully met their air quality compliance standards.

The ideal roadmap approach or critical mass program is to capture all activities and efforts needed by both corporate and operating units to assess, prevent, respond, permit and control air emissions from the entire POTW's wastewater collection and treatment system. This conceptual program is currently not clearly defined at any one POTW in the world, but implementation of many of the following elements should be considered when evaluating a POTW's current air quality compliance program.

17.4 ROADMAP MAJOR AIR QUALITY CONTROL PROGRAM ELEMENTS

For an "average" air quality compliance program, FTEs must be spent or distributed according to the following task per each functional organization inside the POTW. Corporate or operating units need to decide who leads and who provides secondary support and then make roles and responsibilities match the compliance process. Basic elements include:

- Process monitoring and control
- Recordkeeping and reporting
- Preventive and corrective maintenance
- Regulatory interactions and odor compliant response
- Compliance investigation and follow-up
- Process optimization
- Research, special studies, troubleshooting and emissions characterization
- Planning, design and construction
- Administrative activities

17.4.1 Process Monitoring and Control

Task activities include air quality compliance sampling and monitoring (daily, weekly, monthly or annually), documenting compliance equipment operation and chemical or combustion gas usage, calibrating and spanning monitoring equipment to ensure accurate readings, and daily inspections of abatement equipment and associated equipment, tanks or pipes.

17.4.2 RECORDKEEPING AND REPORTING

Task activities include compliance data compiling and submission, QA/QC review of any air quality-related compliance data including monitoring and source test results, fuel usage, hours of operation of combustion devices, down time of equipment contributing to emissions, annual VOC emissions estimates, maintaining a compliance database and reporting process, reviewing operating and maintenance (O&M) reports and compliance strategy implementation or completion and tracking O&M equipment routine maintenance and calibration needs, complaints and follow-up activities, etc.

17.4.3 PREVENTIVE AND CORRECTIVE MAINTENANCE

Task activities include abatement equipment and associated components routine preventive and corrective maintenance (PM and CM), routine inspections and abatement equipment adjustments and corrections, calibrating and cleaning sampling and monitoring probes and connections and verifying that equipment is operating as designed or required to meet compliance requirements.

17.4.4 REGULATORY INTERACTIONS AND ODOR COMPLAINT RESPONSE

Task activities include escorting regulatory agency staff on all planned and unplanned site and records inspections, responding to regulatory information and permitting requests, completing regulatory surveys and required documentation for compliance, responding to odor complaints (i.e., calling back the complainer and following up with O&M to determine odor cause and prevention approaches), completing documentation and reporting and proactively interfacing with air quality regulatory agencies on any proposed new or modified laws and regulations that could impact POTWs.

17.4.5 COMPLIANCE INVESTIGATION AND FOLLOW-UP

Task activities include investigating compliance-related issues, upsets or breakdowns and violations; completing technical review of noncompliance events and passing documentation to the appropriate regulatory agency or management staff; reviewing abatement equipment performance and corrections taken to keep it in compliance; looking for patterns or the end of the useful life of the equipment or monitor and incorporating findings into a database and issuing follow-on correction policies, O&M requests or new equipment needs.

17.4.6 PROCESS OPTIMIZATION

Task activities include reviewing process data and looking for ways to optimize compliance by optimizing abatement equipment and its design and set points, adjusting set point to reflect loadings and trends, identifying areas of waste and over-compliance, developing strong communications with O&M to look for ways to optimize process controls and abatement equipment and implementing improvements.

17.4.7 Research, Special Studies, Troubleshooting and Emissions Characterization

Task activities include implementing viable research-related projects aimed at optimizing or providing better control of processes that either emit or control air quality emissions, conducting special O&M studies related to optimizing O&M and process- or monitoring-related studies, assessing directly measured air emission from various sources vs. using default emission factors developed from similar sources and assisting engineering to evaluate new but unproven abatement equipment or new processes that emit lower VOC or odor emissions.

17.4.8 Planning, Design and Construction

Task activities include implementing the POTWs capital improvement plan (CIP) with input and needs associated with complying with federal, state and local air quality laws and regulations; determining air quality permit needs and requirements; attaining air quality permits; providing O&M support and equipment upgrades and replacements that meet air quality compliance requirements and designing and constructing abatement equipment that meets air quality regulatory requirements.

17.4.9 Administrative Activities

Task activities include managing the POTW to ensure air quality compliance is continuously maintained; preparing adequate budgets for O&M, CIP, and fiscal that reflect an integrated approach in dealing with air and odor emissions permitting and controls; managing staff and implanting core facility values that reflect a compliant air quality program and reviewing and approving all regulatory correspondence, air quality permits, and purchases and chemicals related to the air quality compliance program.

17.4.10 Determining General FTE Requirements

To facilitate the determination of general FTE requirements, Appendix III presents a template for a table that lists Air Quality Program Elements by Task and Functional Organizational Units. This template lays out the program elements and associated general function groups inside a POTW (less than 50 mgd). The template can be used during an FTE-related audit associated with each program element per corporate or operating unit activities and focus. When completed, the table can be compared with the Best Management Practices (BMPs) table (Table 17.1) to determine gaps or needs, or obtain assurance that the existing air quality compliance program meets or exceeds current BMPs. Typically, the costs associated with FTEs and the overall air quality compliance program can be determined very easily by examining current budget and workload documentation and completing focused audits or interviews to fine-tune FTE or cost estimates.

17.4.11 CORRELATING BEST MANAGEMENT PRACTICES

As mentioned above, the data gathered by a POTW and consolidated in the template table can be benchmarked against data from peer POTWs that were compiled to present BMP levels of effort in FTEs/mgd (Table 17.1). BMPs were determined through an auditing and survey program conducted by the authors that collected program related FTEs and costs for a wide range of POTWs sizes (1 to 100 mgd POTWs). Larger POTWs, with flows greater than 100 mgd, need to assess the total FTEs dedicated by the smaller POTW and develop their own ratios to ensure total compliance per each program element.

Figure 17.1 provides a "critical mass" graph of needed FTEs for a fully compliant program for POTWs greater and smaller than 50 mgd. This figure is an approximation that will need to be ground-truthed against the individual POTW's current compliance status, existing air quality compliance and documentation programs, complexity of air emission sources or permits, regulatory program and permit type and interactions or response needs with local, state and federal regulatory agencies. For example, more FTE effort is needed for a POTW that has more than 100 air quality operating permits, is a Title V major source and handles (risk management plan [RMP] substances above trigger levels. On the other hand, a POTW may subtract FTE needs if it is small or large and has a few air quality permits, is not a Title V Major Source and does not handle RMP-regulated substances above trigger levels. If a POTW is operated under a federally enforced standard operating permit (FESOP), the FTEs can be adjusted to some intermediate values.

17.5 AIR QUALITY COMPLIANCE PROGRAM CASE STUDY

Over the past 10 years, a fictitious POTW "ECHO" has had an acceptable air quality compliance track record with very few permit violations and fewer air quality agency inspections and seems to be handling most permitting and inventory requests well. However, this POTW is facing a new expansion project because its equipment is nearing the end of its useful life. Although new environmentally friendly biotechnology to control air emissions is available, the POTW is faced with chemical costs, operator safety needs, encroachment by several new communities and their activism and potential regulatory standards focused on odor, public nuisance and health laws. Hence, ECHO will be required to spend more time and money to assure continued good air quality-related compliance in the future.

Over the course of the past year, POTW ECHO staff has been working on identifying ways to improve, optimize and use existing capital investments to maintain or improve the coordination and implementation of the roadmap approach to air quality compliance on a corporate and operating unit basis. The first step was to complete an audit — on both a corporate and operating unit basis. This task included interviewing over 85% of POTW ECHO staff and performing numerous site visits and record reviews. This was followed by a benchmarking effort to see how POTW ECHO's air quality program compared with a select peer group of similar wastewater treatment agencies. The interviews and benchmarking showed ECHO's strengths

TABLE 17.1
Best Management Practices (BMPs) POTWs Level of Air Quality Compliance Program Efforts Per Each Program Element in FTEs/MGD for Less Than 50 MGD

Program Element	Operations	Maintenance	Planning and Design Engineering	Administration	Source Control	CIP Engineering	Construction Management	Process Engineering	Internal Auditors	Research Projects
Process Monitoring and Control										
Daily, weekly, monthly and annual sampling	0.1	0.02						0.05		
Abatement equipment checks	0.02	0.1	0.02					0.01		
Calibrate and span monitors	0.02	0.1								
Document chemical and fuel usage	0.02	0.002	0.01					0.01	0.02	
Recordkeeping and Reporting										
Collect compliance data	0.02	0.02	0.02	0.01						
Format and update compliance database	0.02	0.02	0.01					0.02		
QA/QC database	0.02	0.02	0.02					0.02	0.02	
Maintain database	0.02	0.02	0.01					0.02		
Provide compliance data and reports	0.01	0.01	0.02					0.02	0.02	

Preventive and Corrective Maintenance									
Conduct PM per equipment specifications	0.01	0.1							
Conduct CM, as needed	0.05	0.1							
Target compliance equipment for highest cm and pm activities	0.01	0.02	0.02					0.02	
QA/QC any PM or CM		0.02	0.02					0.05	0.01
Maintain monitoring systems and equipment	0.1	0.09							
Regulatory Interactions and Odor Compliant Responses									
Handle regulatory tours and information requests	0.01		0.01	0.01	0.02			0.02	
Follow-up with regulatory agencies	0.01		0.01						
	0.02				0.01				
Track new, pending or modified AQ laws and regulations that impact POTWs	0.02		0.01		0.02				0.01
Develop and implement odor complaint phone and response program	0.02		0.02						
Conduct perimeter odor survey and measurements	0.1								

TABLE 17.1 (CONTINUED)
Best Management Practices (BMPs) POTWs Level of Air Quality Compliance Program Efforts Per Each Program Element in FTEs/MGD for Less Than 50 MGD

Program Element	Operations	Maintenance	Planning and Design Engineering	Administration	Source Control	CIP Engineering	Construction Management	Process Engineering	Internal Auditors	Research Projects
Implement response program and follow-up	0.01				0.01			0.01		
Document and track regulatory requests and odor complaints	0.01			0.01	0.02				0.02	
Compliance Investigation and Follow-up										
Investigate regulatory issues or odor complaints	0.01		0.01					0.01	0.01	
Develop responses and issue	0.01	0.01	0.01					0.02		
Take corrective actions on policy, equipment, or practice based on investigation	0.02	0.02	0.01					0.01		
QA/QC investigations and tools used			0.01					0.01		
Provide both written and verbal responses	0.01	0.01	0.01	0.01				0.01	0.01	

Process Optimization									
Conduct optimization sampling and process investigations	0.01	0.01			0.02	0.01		0.01	
Adjust process and abatement equipment set points	0.01	0.05	0.01			0.01			
Identify process compliance problem areas and implement correction program	0.01	0.02	0.01			0.01		0.05	
Communicate with O&M on optimization changes	0.01					0.02		0.02	
Implement process optimization changes, policies, practices or equipment	0.05	0.05	0.01			0.02	0.1	0.05	0.02
Research, Special Studies, Troubleshooting and Emissions Characterization									
Conduct, as needed, research and special studies to characterize air emissions and viable abatement approaches	0.01	0.01	0.01		0.01	0.01		0.01	
Review CIP projected projects and process optimization activities for research or innovative abatement needs or approaches	0.01	0.01	0.01			0.1		0.01	

TABLE 17.1 (CONTINUED)
Best Management Practices (BMPs) POTWs Level of Air Quality Compliance Program Efforts Per Each Program Element in FTEs/MGD for Less Than 50 MGD

Program Element	Operations	Maintenance	Planning and Design Engineering	Administration	Source Control	CIP Engineering	Construction Management	Process Engineering	Internal Auditors	Research Projects
Track current and pending abatement equipment, compliance monitoring devices that can be viable to the POTW	0.01	0.01	0.01	mu				0.02		
Planning, Design and Construction										
Determine air quality permitting needs and compliance trigger levels or requirements	0.01		0.02			0.01		0.01	0.01	
Attain air quality permits			0.1					0.01	0.01	
Include air quality monitoring, abatement needs and compliance databases into planning and design						0.01		0.01		
Ensure abatement equipment is installed correctly	0.01	0.02	0.1			0.01	0.02	0.01		

Turnover abatement equipment needs and operational requirements to O&M	0.01	0.01	0.02			0.01	0.01
Administration Activities							
Budget for air quality compliance needs — capital, chemical and staffing	0.01	0.01		0.01			0.01
Budget for O&M air quality compliance needs	0.01	0.01		0.01			0.01
Implement POTW's air quality compliance policy and track compliance in organization		0.01	0.01		0.01		0.01
QA/QC compliance documentation and correspondence with regulatory agencies			0.01				
Provide air quality related training and safety awareness	0.02	0.02		0.01			0.01
Budget for air quality permit renewal costs	0.01	0.01		0.01			0.01
Grand Total = 3.65 FTEs							

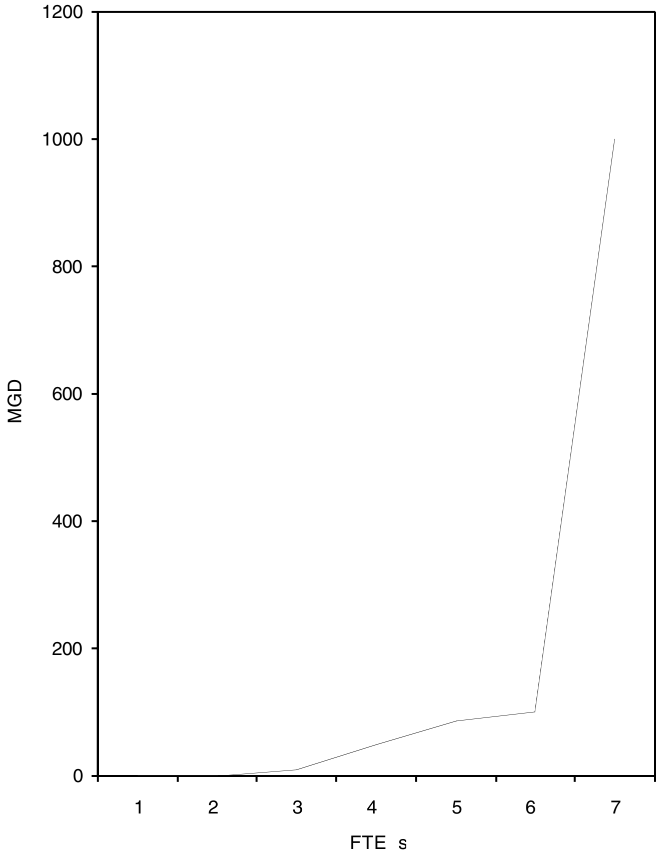


FIGURE 17.1 FTE (full time equivalents) for critical mass air quality compliance program.

and weaknesses both internally and externally. In addition, this benchmarking effort allowed the POTW to build upon successful programs and not reinvent its program to handle current and future needs.

The benchmarking results and the audit confirmed that a successful, good, complete program contains the program elements defined in Section 17.4. These main elements and subtasks cross both corporate and operating units; there is an implied responsibility to meet air quality program requirements to prevent violations, permitting issues and community impacts.

ECHO started to see more awareness due to odor-related issues at its unit processes and collection system. As a consequence, this air quality program effort was realized and completed. POTW ECHO has a very strong base to build upon to develop a good, complete program. Based on the audits, interviews and benchmarking, the following key recommendations are provided to develop a good, complete air compliance program. These recommendations will improve the program to match peer average implementation and FTE levels and provide greater likelihood that POTW ECHO can respond to issues related to the prevention of air quality deterioration or control requirements and service reliability or handling of future air emissions monitoring.

17.5.1 Establish Responsibilities for Air Quality Assessment, Prevention, Response and Control

- Identify and assign key corporate and operating unit managers responsible for complete air quality program implementation. This includes attaching performance-based standards to assess managers' performance plans for raises and bonuses. This will ensure a trickle-down effect to the lowest staff levels and remove the volunteerism seen regarding meeting program needs. This also may trigger redirecting existing staff or hiring staff to handle the many air- and odor-emissions monitoring or control functions at the plants and in the collection system.
- Develop and communicate a written air quality policy to establish the framework for the roadmap program. This requires key corporate and operating unit managers to endorse and sign the air quality policy.
- Define air quality assessment, prevention, response and control responsibilities at the corporate and operating levels, both at the plants and in the collection systems and from the top down to the lowest linking staff. Implement new training programs, if needed, to execute the procedures and policies that will be used to meet regulatory agencies requirements and provide good-neighbor status regarding odors and offsite odor impacts.
- Develop interdepartment and division work plans that proactively guide efforts regarding air quality compliance and assure good coordination among departments in corporate and operating units. This work plan should include determining level and impacts of outside consultants. Also, provide adequate time during shift changes for operating units to do a formal air quality-related turnover from the outgoing staff to the oncoming staff. In addition, evaluate the need for more staff during the off-shift to ensure that air emissions control measures can be monitored, fine tuned and maintained in addition to the other operating requirements.
- Implement BMP-level FTEs at POTW ECHO for the primary elements in a successful air quality compliance program.

17.5.2 Give Priority to a Focused District Wide Air Quality Assessment, Prevention, Response and Control Program That Matches Routine Good-Neighbor Actions

- Focus additional attention on corporate and operating units' communication, training and responsibilities that implement the air quality program throughout that typically matches POTW ECHO's board importance and good-neighbor actions routinely taken.
- Continue to provide employee training and continuing education about air quality assessment, prevention, response and controls — especially in

the areas of research, measurement, chemical handling and usage, maintaining control equipment and odor control strategies and approaches throughout both corporate and operating units.

- Continue cross-functional corporate and operating units working groups that meet to discuss near- and long-term operations and planning efforts and the projects included in these plans, O&M needs and suggested changes that could have air quality impacts. Provide clear guidance on each group's decision power to make or implement changes that are primarily focused on air quality-related activities and needs.
- Set up and maintain a database for air quality assessment and controls for tracking, chemical needs or patterns, sampling data and trends and equipment key operating information.
- Strengthen the air quality compliance program with new hires or interdepartmental transfers to meet current and projected workload associated with full program implementation at both corporate and operating unit levels. Project workload in two ways: (1) using current POTW ECHO staffing approach for projected plant expansions and projects and (2) using BMPs followed by POTW ECHO's peer wastewater treatment facilities. Based on this analysis, POTW ECHO may need to redirect existing staff or hire FTEs related to the air quality compliance program needs.

17.5.3 CONTINUE SUPPORTING POTW ECHO AS A LEADER IN AIR QUALITY ASSESSMENT, PREVENTION, RESPONSES AND CONTROLS

- Continue expanding and improving air quality assessment and control services and capabilities at all levels. Provide cross-staffing and training opportunities to staff to learn about the ways in which air emissions and odors are generated and addressed by the plant, collection system and maintenance group.
- Coordinate work efforts of several similar functional teams in corporate and operating unit to better manage all aspects of the program. Continue looking at activities that assess current, pending and future air emissions-control requirements, programs, air district's responses and impacts over a 20-year window. Ensure that plant expansions and new projects have proper air quality and control considerations early in the planning and design cycle, and use qualified outside consultants who know and understand the needs and the importance that POTW ECHO places on them.
- Continue supporting outreach activities to industry professional associations that help better the knowledge on air emissions and odor assessment, prevention, responses and controls. Work with these groups to achieve better air quality permit and compliance requirements. Continue to seek and maintain leadership positions in key panels and committees to portray a proactive structure that would give leverage in shaping emerging laws and regulations related to air quality compliance and permits.
- Advocate a "good-neighbor activities make good policy" strategy in day-to-day and long-term activities and planning. Look at cost-effective

measures and checks and balances that ensure that POTW ECHO's mission is met while reducing or eliminating air emissions and odors.

17.5.4 Use Incident Command System To Respond to Air Quality Permit Violation or Breakdown Event

Use incident command system to mobilize corporate and operating unit staff to respond to air quality permitting incidents or odor complaints, or in response to a potential offsite impact caused by an air abatement equipment breakdown. This will assure faster, more coordinated actions to remedy problems and to expeditiously respond to the regulatory agency. This approach also empowers all levels of staff to implement the corrective action systems based on observed conditions at the plants and in the collection systems. From observations seen at peer wastewater treatment facilities that have this approach, major air quality-related events are handled effectively and quickly and most potential offsite odor and other emission events observed by onsite staff are addressed and prevented from going offsite.

17.6 IMPLEMENTING THE ROADMAP AT POTWS OF ANY SIZE

For POTWs less than 50 mgd, a rule of thumb based on the combined experiences of the authors is that FTEs needed to ensure an average air quality compliance program are roughly equal to 0.21 FTE per mgd of wastewater. This FTE figure is generally broken down as 0.07 FTE per mgd for air quality compliance and 0.14 FTE per mgd for odor-related program needs over a wide spectrum of functional groups, departments, divisions or teams in the POTW organization. For POTWs larger than 50 mgd, the rule of thumb needs to be adjusted downward and be in line with the total effort to implement all the elements in the roadmap approach. Figure 17.1 is based on 0.07 FTE for a fully compliant air quality compliance program and not 0.21 mgd for a program that also handles odors assessments and controls.

However, based on the authors' experience, most U.S. POTWs will need to add or redirect the activities of their current FTEs into various air quality-related functions that are spread out in the organization to develop a good, complete air monitoring and control program for their plants and collection systems. The 0.07 FTE per mgd is the average FTE/mgd ratio seen from several fully air quality compliant POTWs in the U.S. at less than 50 mgd.

This analysis used several tools, including staff interviews, POTW surveys, actual organization experiences and general observations made at several POTWs across the world. Many barriers inside these POTWs and others prevent full implementation of an optimized air quality compliance program. Thus, the 0.07 FTE per mgd should be viewed as the ideal level to attain for the best-in-class regarding air quality compliance.

A compliant air quality program is only as powerful as its "compliance policy" and direction from its board of directors.

Table 17.2 shows the program elements and where the reader can find information about each element elsewhere this book, plus a guide of what is important for

TABLE 17.2
Roadmap Program Element

Process Monitoring and Control Chapters/ Subsections	Recordkeeping and Reporting Chapters/ Subsections	PM and CM Chapters/ Subsections	Regulatory Interactions and Odor Complaint Response Chapters/ Subsections	Compliance Investigations and Follow-up Chapters/ Subsections	Process Optimization Chapters/ Subsections	Research Chapters/ Subsections	Planning, Design and Construction Chapters/ Subsections
2.1	2.1	2.4	2.2	2.1	4.1	2.4	2.2
2.2	2.4	5.8	2.3	2.4	4.2	2.5	2.4
2.3	2.5	12	2.4	2.5	4.3	5.5	3.2
2.4	4	13	2.5	12	5.2 – 5.7	6	4
2.5	5	14	2.7	14	6	7	5.8
3.2	6	15	3.3	17	7	8	6
4.4	12		5.1		8	9	7
4.5	13		6		9	10	8
5			7		10	11	9
6			12		11	12	10
7			13		13	13	11
8			15		15	14	12
9						15	13
10							14
11							15
12							
13							
14							

Key Words:	**Key Words:**	**Key Words:**	**Key Words:**	**Key Words:**	**Key Words:**	**Key Words:**	**Key Words:**
Emission Equations	Compliance	Case Studies	Permits	Monitoring	Processes	Biotechnology	Regulations
Monitoring	Documentation	Operation	Reporting and Records	Investigations	Wastewater	Controls	Processes
Processes	Measurement methods	Construction needs	Measurement	Responses	Biosolids	Models	Controls
Wastewater	Clean air act	Space needs	Monitoring	Programs	Combustion	Processes	Costs
Biosolids	Permits		Responses		Measurement	Sampling	Design parameters
Combustion			Regulatory agencies		Models	Measurements	Needs
			Laws and regulations		Parameters	Gaps/needs	Gaps
					Needs	Innovative	Measurement
						Emerging	Monitoring

the reader to focus on while exploring the information held in each chapter. This table applies to all POTWs.

Figure 17.2 shows the effort and understanding needed to build awareness for a fully compliant air quality program at a POTW. As shown in the figure, the level of understanding of air compliance issues increases up to a point with the effort (FTEs or mgd) expended and it remains stationary beyond a point, which is the critical mass point for the particular POTW. Also, the awareness of all plant personnel including those not directly involved in air quality compliance issues and the community will also increase in step with the effort. However, the awareness usually continues to increase at a slower rate with an increase in effort beyond the critical mass point and then becomes stationary beyond a certain effort level. This figure can be reversed to show that cost and compliance benefits drop and grow, respectively, as awareness grows and becomes "mainstream" within the organization.

17.7 SUMMARY

In implementing a fully functional air quality and compliance program, a POTW has a number of resources on which to draw. Lessons learned by other POTWs provide valuable insight, including the appreciation of the significance of site-specific factors, such as size, location, degree of industrial waste discharged to the system and unit processes employed. In order to maintain a well-operated and

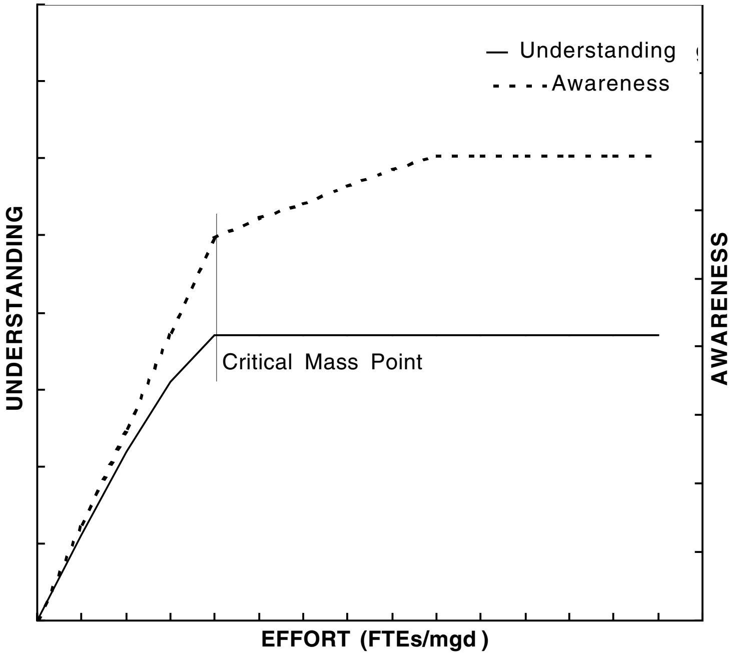


FIGURE 17.2 Conceptual representation of effort, understanding and awareness pertaining to air emissions control and compliance at POTWs.

maintained treatment plant that satisfies all the air quality requirements, in terms of both VOC and odor control, a certain minimum amount of effort in terms of allocation of human and material resources (or “critical mass”) should be made. The critical mass required will vary from plant to plant, but rules of thumb developed for POTWs less than 50 mgd can be scaled up or scaled down to apply to plants as small as 1 mgd or as large as 1 billion gallons per day.

Because even the “best” air quality compliance programs require some fine tuning and adjustments, a roadmap approach is recommended to assess, plan, develop and implement successful, fully compliant programs. To use the roadmap, each POTW will need to evaluate its current resources and practices quickly, while focusing on assessing the functional organization and then evaluating and recommending improvements. The basis for this assessment is a conversion of the POTW’s dedicated or part-time air quality-related compliance staff into FTEs performing diverse functions in various departments.

Key steps in the roadmap approach are performing an internal audit of the existing program, benchmarking against peer agencies, identifying the components of a viable roadmap and providing resource estimates to implement a fully compliant air quality program.

A useful tool in developing the roadmap is a template table listing air quality program elements by task and functional organizational units that can be filled out with POTW-specific information and benchmarked against data from peer POTWs. The peer data present BMP levels of effort in FTEs/mgd. Using a “critical mass” FTE graph as a supplemental analytical tool, an individual POTW can determine an FTE approach for its own unique requirements.

When the proper roadmap is in place, POTW managers can also use it in their outreach activities to convince the public that management is responsive to their concerns and needs.

Appendix I

TOP-DOWN RACT EXAMPLE AND WORKSHEETS

EXAMPLE NO. 1 WORKSHEET 1-1
Definition of Process Requirements

Applicable Regulations

Air Pollution Control District-New Source Review
BACT, Emission Offsets

Pollutants of Concern

Total VOC

Definition of Control Technology Acceptance

Agreed between BAAT City Air Agency and Clear Water Creek to consider each applicable control technology regardless of acceptance criteria rating.

Cost Effectiveness Criteria ($/ton)

$20,000/ton VOC

Performance Criteria (ppm, percent reduction, tons reduced, tons per year allowed)

Minimum of 90% VOC control efficiency (overall project)

Risk Criteria

Not applicable

Thresholds/*De Minimus* Values

1 lb/day VOC

Approach/Level of Detail

EPA Top-Down BACT Process

Guidance and Comments

Applicable Regulations: Pertinent air quality and, in some cases, other environmental regulations, should be listed here. For the example, it is assumed BACT is the principal requirement.

Pollutants of Concern: Each specific toxic air contaminant and VOC should be listed here if it is required to be analyzed by a specific regulation. For the example, it is assumed that only total VOCs are required for analysis.

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

EXAMPLE NO. 1 WORKSHEET 1-1 (CONTINUED)
Definition of Process Requirements

Definition of Control Technology Acceptance: The space is provided to include the minimum control technology acceptance criteria for a specific application and regulation(s). These criteria are provided in Section 4.2. For the example, it is assumed that all applicable control technologies listed in the document should be analyzed.

Cost Effectiveness Criteria: If a local air agency has cost-effectiveness criteria, they should be listed here. For the example, it is assumed that a $20,000/ton criteria has been provided by the local air agency. In many cases, the cost is greater than this criteria. If so, the technology may be eliminated from further analysis.

Performance Criteria: In many cases, local air quality agencies require a specific emission reduction level to meet BACT or another regulation. For the example, it is assumed that a 90% VOC control efficiency (minimum) for the project is required to meet BACT.

Risk Criteria: Not applicable since a Top-Down BACT analysis has been undertaken.

Thresholds/*De Minimus* Values: This space is provided to include a threshold emission level for an applicable regulation. For the example, a 1 lb/day VOC threshold is assumed. If VOC emissions from one or more of the new emission sources are less than 1lb/day, then the BACT analysis would not be required. For the example, each new source has an uncontrolled VOC emission level greater than 1 lb/day.

Approach Level of Detail: This space in the form is to define what approach or methodology and level of detail is to be used to select emission controls. For the example, it is assumed an EPA top-down process is required.

EXAMPLE NO. 1 WORKSHEET 2-1
Facility Description and Flowsheet

Facility Name and Description

Clear Water Creek Water Reclamation Facility

Major Characteristics

Level of Treatment Provided: *Secondary Reclamation*
Flow: *60 mgd (will be increased to 120 mgd)*
Industrial Contribution: *Minor, <10%*
Population Served: *1 million*

Project Description with Optional Flow Diagram

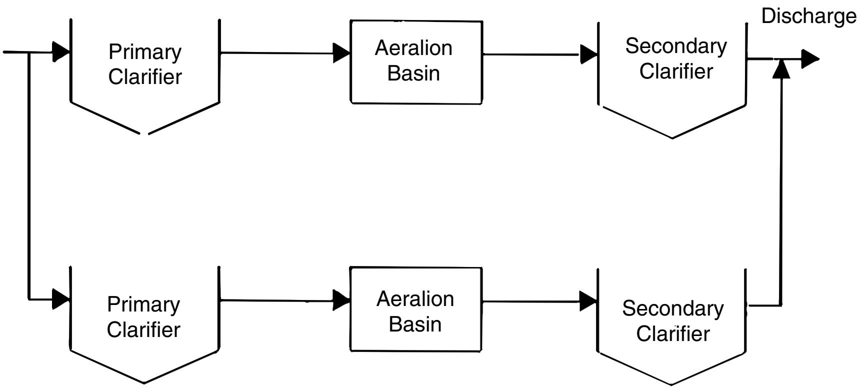
Expand facility from 60 to 120 mgd average dry weather flow (ADWF)
Primary sedimentation surface area—46,200 ft^2
Secondary clarifier surface area—85,700 ft^2
Diffused air activated sludge basin—135,000 ft^2

Guidance and Comments

Facility Description and Location: Self Explanatory

Major Characteristics: Space has been provided to describe the major process components of the facility. An industrial contribution space is also included so that industrial organic usage and discharge may be addressed if applicable.

Project Description: This part of the worksheet is fairly self explanatory. The provided surface areas for the new primary clarifier, diffused air activated sludge basin, and secondary clarifier are based on typical applications. It is recommended to include a simplified (handwritten) process flow diagram in the space provided. This diagram will help the user understand the overall process.



EXAMPLE NO. 1 WORKSHEET 2-2
Emission Source Descriptions

	Source Name	**Source Name**	**Source Name**	**Source Name**	**Source Name**	**Source Name**
	Primary Sedimentation (uncovered)	**Diffused Air Activated Sludge**	**Secondary Clarification**			
Description						
Size	*60 mgd (new)*	*60 mgd (new)*	*60 mgd (new)*			
# of Units	*8 (4 new)*	*8 (4 new)*	*8 (4 new)*			
Percent of plant flow	*50%*	*50%*	*50%*			
Covered/vented	*Open*	*Open*	*Open*			
ID Number						
Source	*001*	*002*	*003*			
Abatement device	*None*	*None*	*None*			
Point/fugitive	*Fugitive*	*Fugitive*	*Fugitive*			
Estimated Emissions						
Total VOCs	*2,400 lb/yr*	*11,400 lb/yr*	*720 lb/yr*			
Volatile/degradable						
Xylenes						
Toluene						
Benzene						
Ethylbenzene						
Volatile/non-degradable						
Methylene chloride						
Tetrachloroethylene						
1,1,1-Trichlorethane						
Chloroform						
Non-volatile/degradable						
MIBK						
MEK						
Acetone						
Estimation methods	*Flow-based EF (lb/yr/mgd)*	*Flow-based EF (lb/yr/mgd)*	*Flow-based EF (lb/yr/mgd)*			
Baseline risk screening results (optional)						
Air stream						
Concentration						
Rate	*10-100 ppm*	*1-10 ppm*	*0-2 ppm*			

EXAMPLE NO. 1 WORKSHEET 2-2 (CONTINUED)
Emission Source Descriptions

Guidance and Comments

Description: Spaces have been provided to record the size, number of units, and percent of plant flow for the new or modified emission sources. For the example, 50% of the expanded facility now (120 mgd) goes through the three new sources.

Covered/Vented: Self Explanatory

ID Number: Spaces have been provided for emission source number, abatement device, and whether a source is a point or fugitive source. The source number may be a plant number or an air agency-assigned number. A point source is a source with a defined vent or stack. Other sources are fugitive. For the example, the three new sources are open area sources and therefore are categorized as fugitive sources. The current design for these emission sources does not include emission control devices.

Estimated Emissions: Estimated emissions should include the baseline emission rate for each new or modified source prior to BACT determination or other control technology determination process. Baseline emissions may be uncontrolled or current emissions from a source. Consultation with your local air agency would be needed to define baseline emissions. The emissions in the example are uncontrolled emissions and are calculated from the emission source description data sheets located in Section 3.4. These data sheets provide flow-based emission factors in units of lb/yr/mgd. Multiplying the flow through each source (60 mgd in the example) by the emission factor results in the recorded baseline emission rates.

Estimation Methods: The emission estimation method used in the example was flow-based and was provided in the emission source description data sheets. The data sheets also provide concentration-based emission factors that can be used if measured influent concentrations are known.

Baseline Risk Screening Results (Optional): This space has been provided to incorporate the results of a baseline risk screening analysis. Baseline risk is usually defined as risk from uncontrolled project emission sources. This risk screening is not applicable for a top-down BACT determination,

Air Stream: Air stream concentrations can also be obtained from the emission source description data sheets. The concentrations used in the example were obtained from these data sheets.

*Data are for project (modified or new) emission sources

EXAMPLE NO. 1 WORKSHEET 3-1
Preliminary Control Technology — Evaluation and Rating

Technologies	Source I.D. # 001	Source I.D. # 002	Source I.D. # 003	Source I.D. #	Source I.D. #
Air Stream Concentration	10-100 ppm	1-10 ppm	0-2 ppm		
Traditional Vapor Phase					
Thermal-No Heat Recovery	L1	L1	L1		
Thermal-Heat Recovery	L1	L1	L1		
Thermal-Catalytic	L1	L1	L1		
Activated Carbon	L1	L1	L1		
In situ Regenerative Activated	L1	L1	L1		
Carbon	L1	L1	L1		
Nontraditional Vapor Phase					
Soil Filters	U	U	U		
Process Air Recycle	U	U	U		
Atomized Mist	U	U	U		
Packed Towers	U	U	U		
Containment					
Passive	L1	L1	L1		
Vented/Occupied	L2	L2	L2		
Vented/Nonoccupied	L2	L2	L2		
Process and Practices					
Turbulence Reduction	U	U	U		
Operational Changes	U	U	U		
Wind Break	L1	L1	L1		
Process Substation	U	U	U		
Industrial Pretreatment	U	U	U		
Product Substitution	U	U	U		

Other Controls

Guidance and Comments

Air Stream Concentration: Air stream concentrations are provided in the emission source description data sheets in Section 3.4. The example used the concentrations provided in these data sheets.

EXAMPLE NO. 1 WORKSHEET 3-1 (CONTINUED)
Preliminary Control Technology — Evaluation and Rating

List of Potential Control Technologies: The primary purpose of this worksheet is to rate each potential control technology according to the rating criteria codes summarized in Section 4.2 (Tables 4.1 and 4.2). Each potential control technology (control technologies listed on the worksheet or new or updated control technologies added to the worksheet) should be assigned a rating criteria code or evaluated and rated using site-specific data if available. The example lists the rating criteria codes listed in Table 4.2. Since it was decided (in Worksheet 1-1) to evaluate all control technologies listed in the document regardless of criteria code, each control technology should be carried forward into the feasibility evaluation (Worksheet 4-1).

* Assign control technology rating criteria codes (from Table 4.2.2 of Section 4.2) for each source and control option. If additional site-specific data are available, they should also be used in the evaluation.

EXAMPLE NO. 1: WORKSHEET 4-1
Feasibility Evaluation

Evaluation Criteria		Application Description		Expected Performance		Economic Impacts		Energy Impacts		Environmental Impacts		Feasibility Assessment Results	
Control Technology: Covered/Vented (Nonoccupied)													
Application: Primary Sedimentation													
Pollutants	VOCs	Air stream concentration (ppm)	10–100	Emission reduction	Up to 1.1 tpy	Annualized costs ($/yr)	398,000	Fuel type	–	Cross-media impacts		High annualized cost although technically feasible	Carry forward ☐ Discard ☐
Cost Criteria	20,000/ ton	Air stream (cfm)	46,200	Percent reduction	Up to 90%	Cost effectiveness ($/ton)	362,000 min.	Fuel Consumption	–	Solid waste	–		
Performance Criteria (% reduction, tons reduced ppm, tons per year)	90% reduction VOCs (overall project)	Uncontrolled emissions (tpy)	1.2	Controlled emissions	0.1 tpy minimum	Acceptable	Yes ☐ No ☐	Electric demand	1.3 KWH/yr/ cfm = 0.51 Btu/hr/cfm	Waste-water	Potential water quality perform ance impacts		
Allowable risk	Not applicable	Acceptable (Figure 4.21)	Yes ☐ No ☐	Technical limitations	Resolvable ☐ Unresolvable ☐			Acceptable	Yes ☐ No ☐	Secondary emissions	–		
Acceptable energy usage Btu/hr/cfm	2,762									Toxic Emissions	–		
									Risk Screen Results (Optional)	–			
									Acceptable	Yes ☐ No ☐			
Control Technology: Covered/Vented (Nonoccupied)													
Application:Diffused Air Activated Sludge													
Pollutants	VOCs	Air stream Concentration (ppm)	1–10	Emission Reduction	Up to 5.1 tpy	Annualized Cost ($/yr)	$1,162,000	Fuel Type	–	Cross-Media		High annualized cost although technically feasible	Carry forward ☐ Discard ☐

Cost Criteria ($/ton)	20,000/ton	Air stream (cfm)	135,000	Percent Reduction	Up to 90%	Cost-Effectiveness ($/ton)	228,000 minimum	Fuel Consumption	–	Solid Waste	–
Performance Criteria (% reduction, tons reduced ppm, tons per year)	90% reduction VOCs (overall project)	Uncontrolled Emissions (tpy)	5.7	Controlled Emissions (tpy)	0.6 tpy minimum	Acceptable	Yes ☐ No ☐	Electric Demand	1.3 kWH/yr/cfm = 0.51 BTU/hr/cfm	Wastewater	Potential water quality perform ance impacts
Allowable Risk	Not Applicable	Acceptable (Figure 4.21)	Yes ☐ No ☐	Technical Limitations	Resolvable ☐ Unresolvable ☐			Acceptable	Yes ☐ No ☐	Secondary Emissions	–
Acceptable Energy Usage BTU/hr/cfm	2,762									Toxic Emissions	–
										Risk Screen Results (Optional)	–
										Acceptable	Yes ☐ No ☐

Control Technology: Covered/Vented (Nonoccupied)

Application: Secondary Clarification

Pollutants	VOCs	Air stream Concentration (ppm)	0–2	Emission Reduction	Up to .32 tpy	Annualized Cost ($/yr)	738,000	Fuel Type	–	Cross-Media Impacts		High annualized cost although technically feasible	Carry Forward ☐ Discard ☐
Cost Criteria ($/ton)	20,000/ton	Air stream (cfm)	85,700	Percent Reduction	Up to 90%	Cost-Effectiveness ($/ton)	2,306,000 minimum	Fuel Consumption	–	Solid Waste	–		
Performance Criteria (% reduction, tons reduced ppm, tons per year)	90% reduction VOCs (overall project)	Uncontrolled Emissions (tpy)	.36	Controlled Emissions (tpy)	0.04 tpy minimum	Electric Demand	1.3 kWH/yr/cfm = 0.51 BTU/hr/cfm	Wastewater	Potential water quality performance impacts				
Allowable Risk	–	Acceptable (Figure 4-1)	Yes ☐ No ☐	Technical Limitations	Resolvable ☐ Unresolvable ☐	Acceptable	Yes ☐ No ☐	Secondary Emissions	–				
Acceptable Energy Usage BTU/hr/cfm	2,762									Toxic Emissions	–		
										Acceptable	Yes ☐ No ☐	Acceptable	Yes ☐ No ☐

EXAMPLE NO. 1: WORKSHEET 4-1 (CONTINUED)
Feasibility Evaluation

Evaluation Criteria		Application Description		Expected Performance		Economic Impacts		Energy Impacts		Environmental Impacts		Feasibility Assessment Results	
Control Technology: Atomized Mist													
Application: Primary Sedimentation													
Pollutants	VOCs	Air stream Concentration (ppm)	10–100	Emission Reduction	0.07 tpy	Annualized Cost ($/yr)	400,000/yr atomized Mist + 393,000/yr Cover = 743,000/yr	Fuel Type	–	Cross-Media Impacts		Technically feasible, unproven for VOC control, costs are high	Carry Forward ☐ Discard ☐
Cost Criteria ($/ton)	20,.000/ton	Air stream (cfm)	46,200	Percent Reduction	70%	Cost-Effectiveness ($/ton)	635,000	Fuel Consumption	–	Solid Waste	–		
Performance Criteria (% reduction, tons reduced ppm, tons per year)	90% reduction VOCs (overall project)	Uncontrolled Emissions (tpy)	0.1[a]	Controlled Emissions (tpy)	0.03	Acceptable	Yes ☐ No ☐	Electric Demand	6.5 kWH/yr/cfm = 2.5 BTU/hr/cfm	Wastewater	Potential water quality performance impacts		
Allowable Risk	–	Acceptable (Figure 4-1)	Yes ☐ No ☐	Technical Limitations	Resolvable ☐ Unresolvable ☐			Acceptable	Yes ☐ No ☐	Secondary Emissions	–		
Acceptable Energy Usage BTU/hr/cfm	2,762									Toxic Emissions	Potential vapor chlorine leaving system		
										Risk Screen Results (Optional)	–		
										Acceptable	Yes ☐ No ☐		

Control Technology: Atomized Mist

Application: Diffused Air Activated Sludge

Pollutants	VOCs	Air stream Concentration (ppm)	1–10	Emission Reduction	0.4 tpy	Annualized Cost ($/yr)	1,000,000/yr Atomized Mist + 1,150,000/yr Cover = 2,150,000/yr	Fuel Type	–	Cross-Media Impacts		Technically feasible, unproven for VOC control, costs are high	Yes ☐ No ☐
Cost Criteria ($/ton)	20,000/ton	Air stream (cfm)	135,000	Percent Reduction	70%	Cost-Effectiveness ($/ton)	391,000	Fuel Consumption	–	Solid Waste	–		
Performance Criteria (% reduction, tons reduced ppm, tons per year)	90% reduction VOCs (overall project)	Uncontrolled Emissions (tpy)	0.6^a	Controlled Emissions (tpy)	0.2	Acceptable	Yes ☐ No ☐	Electric Demand	6.5 kWH/yr/cfm = 2.5 BTU/hr/cfm	Wastewater	Potential wastewater impact		
Allowable Risk	–	Acceptable (Figure 4-1)	Yes ☐ No ☐	Technical Limitations	Resolvable ☐ Unresolvable ☐			Acceptable	Yes ☐ No ☐	Secondary Emissions	–		
Acceptable Energy Usage BTU/hr/cfm	2,762									Toxic Emissions	Potential vapor chlorine leaving system		
										Risk Screen Results (Optional)	–		
										Acceptable	Yes ☐ No ☐		

Control Technology: Atomized Mist

Secondary Clarification

Pollutants	VOCs	Air stream Concentration (ppm)	0–2	Emission Reduction	0.03 tpy	Annualized Cost ($/yr)	700,000/yr atomized Mist + 729,000/yr Cover = 1,429,000/yr	Fuel Type	–	Cross-Media Impacts		Technically feasible, unproven for VOC control, costs are high	Carry Forward ☐ Discard ☐
Cost Criteria ($/ton)	20,000/ton	Air stream (cfm)	85,700	Percent Reduction	70%	Cost-Effectiveness ($/ton)	4,083,000	Fuel Consumption	–	Solid Waste	–		

EXAMPLE NO. 1: WORKSHEET 4-1 (CONTINUED)
Feasibility Evaluation

Evaluation Criteria		Application Description		Expected Performance		Economic Impacts		Energy Impacts		Environmental Impacts		Feasibility Assessment Results	
Performance Criteria (% reduction, tons reduced ppm, tons per year)	90% reduction VOCs (overall project)	Uncontrolled Emissions (tpy)	0.04^a	Controlled Emissions (tpy)	0.01	Acceptable	Yes ☐ No ☐	Electric Demand	6.5 kWH/yr/ cfm = 2 .5 BTU/hr/ cfm	Wastewater	Potential water quality performance impacts		
Allowable Risk	–	Acceptable (Figure 4-1)	Yes ☐ No ☐	Technical Limitations	Resolvable ☐ Unresolvable ☐			Acceptable	Yes ☐ No ☐	Secondary Emissions	–		
Acceptable Energy Usage BTU/hr/cfm	2,762									Toxic Emissions	Potential vapor chlorine leaving system		
										Risk Screen Results (Optional)	–		
										Acceptable	Yes ☐ No ☐		

Control Technology: Process Air Recycle

Application: Primary Sedimentation

Pollutants	VOCs	Air stream Concentration (ppm)	10100	Emission Reduction	0.08 tpy	Annualized Cost ($/yr)	40,000/yr Process Air Recycle + 393,000/yr Cover = $433,000/yr	Fuel Type	–	Cross-Media impacts		Technically feasible with little environmental or energy impact, costs are high	Carry Forward ☐ Discard ☐
Cost Criteria ($/ton)	20,000/ton	Air stream (cfm)	46,200	Percent Reduction	80% (order of magnitude)	Cost-effective ($/ton)	367,000	Fuel Consumption	–	Solid Waste	Environmentally friendly		

Performance Criteria (% reduction, tons reduced ppm, tons per year)	90% reduction VOCs (overall project)	Uncontrolled Emissions (tpy)	0.1[a]	Controlled Emissions (tpy)	Approximately 0.02	Acceptable	Yes ☐ No ☐	Electric Demand	No additional energy impact	Wastewater	–		
Allowable Risk	–	Acceptable (Figure 4-1)	Yes ☐ No ☐	Technical Limitations	Resolvable ☐ Unresolvable ☐			Acceptable	Yes ☐ No ☐	Secondary Emissions	–		
Acceptable Energy Usage BTU/hr/cfm	2,762									Toxic Emissions	–		
										Risk Screen Results (Optional)	–		
										Acceptable	Yes ☐ No ☐		

Control Technology: Pretreatment

Application: All Sources

Pollutants	VOCs	Air stream Concentration (ppm)	0–100	Emission Reduction	3.7 tpy	Annualized Cost ($/yr)	4,275/yr/mgd = 256,500/yr	Fuel Type	Essentially no energy impact	Cross-Media impacts		A technically feasible and low impact technology, performance difficult to quantify, costs may be a concern to industry	Carry Forward ☐ Discard ☐
Cost Criteria ($/ton)	20,000/ton	Air stream (cfm)	–	Percent Reduction	50%[b]	Cost-Effectiveness ($/ton)	69,300	Fuel Consumption	–	Solid Waste	Very environmentally friendly		
Performance Criteria (% reduction, tons reduced ppm, tons per year)	90% reduction VOCs (overall project)	Uncontrolled Emissions (tpy)	7.3	Controlled Emissions (tpy)	3.7	Acceptable	Yes ☐ No ☐	Electric Demand	–	Wastewater	–		
Allowable Risk	–	Acceptable (Figure 4-1)	Yes ☐ No ☐	Technical Limitations	Resolvable[c] ☐ Unresolvable ☐			Acceptable	Yes ☐ No ☐	Secondary Emissions	–		
Acceptable Energy Usage BTU/hr/cfm	–									Toxic Emissions	–		

EXAMPLE NO. 1: WORKSHEET 4-1 (CONTINUED)
Feasibility Evaluation

Evaluation Criteria	Application Description	Expected Performance	Economic Impacts	Energy Impacts	Environmental Impacts		Feasibility Assessment Results
					Risk Screen Results (Optional)	–	
					Acceptable	Yes ☐ No ☐	

Guidance/Comments

Separate copies of Worksheet 4-1 should be used for each control technology application that meets the previously agreed upon acceptance criteria. To simplify the example, separate worksheets were prepared only for select control technologies that will subsequently be used in the control alternatives. If the given criteria listed in the worksheet is met or the user is not certain, then the "Yes" box should be checked. If the criteria is unacceptable, the "No" box should be checked.

Evaluation Criteria: The evaluation criteria specified in Worksheet 1-1 has been presented here as reference. The acceptable energy usage value presented in each worksheet (2762 Btu/hr/cfm) is based on the combined Btu output from fuel consumption and electric usage in an equal-sized recuperative thermal incinerator without heat recovery. It is assumed that higher energy requirements in a control system are unacceptable.

Application Description: The air stream concentration and uncontrolled emission rates have been brought over from Worksheet 2-2. The emission rates have been converted from pounds to tons. To determine the air stream rate (in cfm), it is assumed that 1 cfm of air is needed for each square foot of source cover. As a result, the air stream flow rate is equivalent to the total cover area. If the air stream characteristics do not meet the guidance provided in Figure 4.1, then the "No" box should be checked. If the air stream characteristics do meet the guidance or if you are uncertain, the "Yes" box should be checked. In each case in the example, the air stream characteristics are acceptable for the corresponding control.

Expected Performance: The emission reduction and controlled emission rates were calculated based on typical percent control efficiencies for each control technology. These control efficiencies were obtained from the control technology data sheets (Section 4.4). In the case of add-on control equipment, the emission reductions and controlled emissions presented are for the add-on equipment alone. Therefore for this portion of the worksheet, baseline emissions include only emissions after source covers and vents have been installed. The preliminary assessment indicated that any technical limitations are resolvable and as a result, the "Resolvable" box was checked for each control technology application. However, for pretreatment, the established performance criteria of 90% may not be met.

Economic Impacts: In most cases, annualized costs were determined directly from cost curves provided in the control technology data sheets (Section 4.4). By knowing the required air flow, one can directly read the annualized cost of control.

Annualized costs for non-occupied covers and vents were based on the equations in the control technology data sheet for this technology (Section 4.4.3.3). The annualized cost calculation assumes a capital recovery factor of 16.28% (typically used in the control cost data sheets provided in the appendix) and an annual maintenance cost equivalent to 5% of the total purchased cost. The annualized electrical usage cost due to fan operation was calculated assuming 2 HP is needed for every 10,000 cfm of air vented. This value was obtained from the control technology data sheet in Section 4.4.3.3. As a result, for the nonoccupied cover and vent applications, the following equation was used to calculate the annualized cost.

(Total purchased cost × 16.28%) + Annual electric cost + (Total purchased cost × 5%, ie., the annual maintenance cost) = Total annualized cost

The annualized cost for the add-on control devices included the annualized cost for covers and vents. The ductwork costs are considered minimal since it is assumed that the add-on devices are adjacent to the source. In addition, the cover cost component of the add-on device cost calculation does not include the fan cost since it has already been incorporated into the add-on device cost curves. The average annualized cost of pretreatment summarized in the control technology data sheet (Section 4.4.4.5) was also used in the example.

Cost-effectiveness was determined by dividing the total annualized cost of control by the tons of emissions reduced. It should be noted that, for each add-on control device (atomized mist, process air recycle), the overall emission reduction was determined from the difference between the uncontrolled emission level (without covers and vents) and the controlled emission level (including emission reductions from both the covers and add-on devices). In each case in this example, the cost-effectiveness values exceeded the cost criteria previously identified. Therefore, since the costs are unacceptable, the “No” box was checked in each case.

Energy Impacts: Fuel consumption and energy demand data was obtained from the control technology date sheets (Section 4.4). If the combined energy usage on an equivalent Btu/hr/cfm basis exceeds the acceptable energy usage, then the technology is not acceptable and the user would put a check in the “No” box on the worksheet. Since the energy usage levels are acceptable in this example, the “Yes” box was checked.

Environmental Impacts: Qualitative information relative to environmental impacts are summarized in the control technology data sheets (Section 4.4). This and any other site-specific information should be summarized on the worksheet. For the example, pertinent environmental impacts from the data sheets are summarized in each worksheet. It is uncertain at this stage whether or not there is a significant or adverse environmental impact for the example. As a result, the “Yes” box was checked for each application of each control technology.

Feasibility Assessment Results: The summary of each control technology feasibility assessment is included here. Pertinent control technology data sheet information on typical performance, applicability, and assessment of current knowledge should also be summarized here. For the example, each control technology application failed to meet the cost-effectiveness criteria of $20,000 per ton and as a result, the “Discard” box was checked, which means that these controls do not meet BACT criteria and should not be selected.

[a] Uncontrolled emissions hee are controlled emissions from Vented Non-Occupied Worksheet.
[b] Above baseline pretreatment program.
[c] However, performance criteria may not be met.

EXAMPLE NO. 1 WORKSHEET 5-1
Control Alternative Development

Alternative No.	Strategy Description	Initial Assessment
1	Covered primary sedimentation with atomized mist, covered diffused air activated sludge and vented/covered, secondary clarifier with atomized mist	High annualized cost-overall control effectiveness difficult to predict. Has been achieved in practice. For odor control systems but not for VOC removal. Potential for production of chlorinated hydrocarbons in atomized mist system.
2	Covered primary sedimendation with process air recycle, covered diffused an activated sludge with atomized mist, uncovered secondary clarifier	High annualized cost associated with atomized mist. Overall control effectiveness difficult to predict. Environmentally friendly
3	Industrial pretreatment	Emission reduction difficult to predict. Potentially costly to industry. Has been achieved in practice. Environmentally friendly.

Guidance/Comments

Control alternatives for each of the THREE emission sources were developed using guidance provided in Section 4.3. A description of these alternatives is provided in this worksheet as well as a summary of the feasibility evaluation information from Worksheet 4-1.

EXAMPLE NO. 1 WORKSHEET 5-2
Alternative Comparison

	Performance			Preliminary Cost Data[b]				
Control Alternative[a]	Emission Reduction Potential (tpy)	Control Level (%)	Controlled Emissions (tpy)	Annualized Cost ($/yr)	Cost-Effectiveness ($/ton)	Risk Level[c]	Regulatory Acceptance Criteria[d]	Preliminary Assessment Comments
1	7.0	97	0.2	3,334,000	476,000	–	BACT, $20,000/ton	Failed cost criteria
2	6.7	92	0.6	2,583,000	386,000	–	BACT, $20,000/ton	Failed cost criteria
3	3.7	50	3.7	256,500	69,300	–	BACT, $20,000/ton	Failed cost criteria

Guidance/Comments

Although each of the control technologies evaluated failed cost criteria, they were carried forward in this example for illustration. The emission reduction potential and controlled emissions presented in this worksheet were calculated for each alternative by summing the individual control technology emission data from Worksheet 4-1. The control cost data presented in this worksheet were also summarized from individual control technology cost data calculated in Worksheet 4-1. If these control alternatives passed this generalized first-cut analysis, then a detailed control alternative analysis would, in all likelihood, be needed to select the final control alternative. Each alternative was listed in descending order with the highest level of control at the top.

[a] If top down BACT process is used, rank each alternative according to control effectiveness, with the highest control effectiveness alternative on the top of worksheet. If the incremental emission reduction procedure is used, rank each alternative according to cost-effectiveness, with the most cost-effective alternative at the top of worksheet.

[b] Generalized cost data obtained from Worksheet 4-1 (Technical Data Sheets in Section 4.4 of this guidance document).

[c] Risk level may be in terms of a risk prioritization score, risk screening level, or refined risk assessment level.

[d] Regulatory acceptance criteria may be in terms of cost-effectiveness, required emissions or risk reduction level, or allowable project emission or risk level.

APPENDIX II

INCREMENTAL EMISSION (RISK) REDUCTION EXAMPLE AND WORKSHEET

EXAMPLE NO. 2 WORKSHEET 1-1
Definition of Process Requirements

Applicable Regulations

Air Pollution Control District Toxic New Source Review
T-BACT

Pollutants of Concern

Methylene chloride, chloroform

Definition of Control Technology Acceptance

Agreed between BAAT City Air Agency and Clear Water Creek to consider each applicable control technology regardless of acceptance criteria rating.

Cost Effectiveness Criteria ($/ton)

Not applicable

Performance Criteria (ppm, percent reduction, tons reduced, tons per year allowed)

Not applicable

Risk Criteria

1E-06 project risk without control
10E-06 project risk after controls

Thresholds/*De Minimus* Values

1E-06 project risk without controls

Approach/Level of Detail

Incremental Emission (Risk) Reduction Process

Guidance/Comments

Applicable Regulations: Pertinent air quality and, in some cases, other environmental regulations, should be listed here. For the example, it is assumed that the incremental emission (risk) reduction process is required.

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

EXAMPLE NO. 2 WORKSHEET 1-1 (CONTINUED)
Definition of Process Requirements

Pollutants of Concern: Each specific toxic air contaminant and VOC should be listed here if it is required to be analyzed by a specific regulation. For the example, it is assumed that methylene chloride and chloroform are the primary drivers of overall project risk.

Definition of Control Technology Acceptance: The space is provided to include the minimum control technology acceptance criteria for a specific application and regulation(s). These criteria are provided in Section 4.2. For the example, it is assumed that all applicable control technologies listed in the document should be analyzed.

Cost Effectiveness Criteria: If a local air agency has cost-effectiveness criteria, these criteria should be listed here. For the incremental risk reduction example, it is assumed that cost-effectiveness criteria are not applicable.

Performance Criteria: In many cases, local air quality agencies require a specific emission reduction level for compliance. For the example, it is assumed that a project risk level without T-BACT of 1E-06 or a project risk level with T-BACT of 10E-06 is required for compliance.

Risk Criteria: A project risk criterion with controls of 10E-06 has been assumed for the example. Many agencies have established risk criteria similar to this.

Thresholds/*De Minimus* Values: This space is provided to include a threshold emission level for an applicable regulation. A de minimus risk level (i.e. project without controls) of 1E-06 is assumed for this example.

Approach Level of Detail: This space in the form is to define what approach or methodology and level of detail is to be used to select emission controls. For the example, it is assumed an incremental emission (risk) reduction process is required.

EXAMPLE NO. 2 WORKSHEET 2-1
Facility Description and Flowsheet

This worksheet does not change from the first example. Refer to Example No. 1 for guidance.

EXAMPLE NO. 2 WORKSHEET 2-2
Emission Source Descriptions

	Source Name	Source Name	Source Name	Source Name	Source Name	Source Name
	Primary Sedimentation (uncovered)	**Diffused Air Activated Sludge**	**Secondary Clarification**			
Description						
Size	*60 mgd (new)*	*60 mgd (new)*	*60 mgd (new)*			
# of Units	*2 (1 new)*	*2 (1 new)*	*2 (1 new)*			
% of Plant flow	*50%*	*50%*	*50%*			
Covered/vented	*Open*	*Open*	*Open*			
ID number						
Source	*001*	*002*	*003*			
Abatement device	*None*	*None*	*None*			
Point/fugitive	*Fugitive*	*Fugitive*	*Fugitive*			
Estimated emissions						
Total VOCs						
Volatile/degradable						
Xylenes						
Toluene						
Benzene						
Ethylbenzene						
Volatile/non-degradable						
Methylene chloride	*6 lb/yr*	*258 lb/yr*	*4.2 lb/yr*			
Tetrachloroethylene						
1,1,1-Trichlorethane						
Chloroform	*3.4 lb/yr*	*282 lb/yr*	*2.3 lb/yr*			
Non-volatile/degradable						
MIBK						
MEK						
Acetone						
Estimation methods	*Flow-based EF (lb/yr/mgd)*	*Flow-based EF (lb/yr/mgd)*	*Flow-based EF (lb/yr/mgd)*			
Baseline risk screening results (optional)	*2.4 E-07*	*1.8E-05*	*1.6E-07*			
Air stream						
Concentration						
Rate	*10-100 ppm*	*1-10 ppm*	*0-2 ppm*			

EXAMPLE NO. 2 WORKSHEET 2-2 (CONTINUED)
Emission Source Descriptions

Guidance/Comments

Description: No change from Example No. 1.

Covered/Vented: Self Explanatory

ID Number: No change from Example No. 1.

Estimated Emissions: Estimated emissions should include the baseline emission rate for each new or modified source before the control technology determination process. Baseline emissions may be uncontrolled or current emissions from a source. Consultation with your local air agency would be needed to define baseline emissions. The methylene chloride and chloroform emissions in the example are uncontrolled emissions and are calculated from the emission source description data sheets located in Section 3.4 of this document. These data sheets provide flow-based emission factors in units of lb/yr/mgd. Multiplying the flow through each source (60 mgd in the example) by the emission factor results in the recorded baseline emission rates.

Estimation Methods: No change from Example No. 1. The emission estimation method used in the example was flow based and was provided in the emission source description data sheets. The data sheets also provide concentration-based emission factors that can be used if measured influent concentrations are known.

Baseline Risk Screening Results (Optional): This space has been provided to incorporate the results of a baseline risk screening analysis. Baseline risk is usually defined as risks from uncontrolled project emission sources. An optional risk screening worksheet (Worksheet 2-3) has been provided to calculate these risks. For the example, risk values from the three uncontrolled emission sources have been calculated in Worksheet 2-3 with results presented here.

Air Stream: Total VOC air stream concentrations can be obtained from the emission source description data sheets. Although specific toxic organic compound concentrations are not provided in the data sheets, total VOC concentrations would be the primary tool needed to determine the overall cost effectiveness of the control options.

* Data are for project (modified or new) emission sources

EXAMPLE NO. 2 WORKSHEET 2-3
Optional Risk Screening

Application: Primary Sedimentation

Risk Screening Methodology

Requires analysis similar to the SCAQMD Rule 1401 (New Source Review of Toxic Air Contaminants)

Pollutants

Methylene chloride, chloroform

Risk Input Parameters (Emissions, Unit Risk Factors, Dipersion Data)

Emissions (Q) = 6 lb/yr (1.6E-02 lb/day) methylene chloride

= 3.4 lb/yr (9.2E-03 lb/day) chloroform

X/Q = 3.633

Unit risk factors: 5.3E-06 (µg/m^3*)*$^{-1}$ *chloroform, 1E-06 (µg/m*^{3}*)*$^{-1}$ *methylene chloride*

Baseline Risk Screening Calculations

MICR= Q × (x Q) × U × MP For VOC, MP = 1

MICR (methylene chloride) = (1.6E-02 lb/day) × 3.633 × (1E-06) = 6E-08

MICR (chloroform) = (9.2E-03 lb/day) × (3.633) × (5.3E-06) = 1.8E-07

Σ MICR = 2.4E-07 risk from primary sedimentation without controls

Risk Screening Calculations (w/Controls)

No controls needed for primary sedimentation

Application: Diffused Air Activated Sludge

Risk Screening Methodology

Requires analysis similar to the SCAQMD rule 1401 (New Source Review of Toxic Air Contaminants)

Pollutants

Methylene chloride, chloroform

Risk Input Parameters (Emissions, Unit Risk Factors, Dispersion Data)

Emissions (Q) = 258 lb/yr (7.1E-01 lb/day) methylene chloride and 282 lb/yr (7.7E-01 lb/day) chloroform

X/Q = 3.633

Unit Risk Factors: 5.3E-06 (µg/m^3*)*$^{-1}$ *chloroform, 1E-06 (µg/m*^{3}*)*$^{-1}$ *methylene chloride*

Baseline Risk Screening Calculations

MICR = Q × X/Q × U × MP for VOC, MP = 1

MICR (methylene chloride) = (7.1E-01 lb/day) × 3.633 × (1E-06) = 2.6E-06

MICR (chloroform) = (7.7E-01 lb/day) × (3.633) × (5.3E-06) = 1.5E-05

Σ MICR = 1.8E-05 risk from diffused air activated sludge without controls

Risk Screening Calculations (w/Controls)

Control Option 1: Cover/vent to atomized mist

Assume 70% emision and risk reduction

Risk with atomized mist = 1.8E-or × 0.3 = 5.5E-06 risk from diffused air system

Control Option 2: Cover/vent to thermal oxidizer with heat recovery

Assume 90% emission and risk reduction

Risk with oxidizer = 1.8-05 × 0.1 = 1.8E-06 risk from diffused air system

EXAMPLE NO. 2 WORKSHEET 2-3 (CONTINUED)
Optional Risk Screening

Application: Secondary Clarification

Risk Screening Methodology

Requires analysis similar to the SCAQMD Rule 1401 (New Source Review of Toxic Air Contaminants)

Pollutants

Methylene chloride, chloroform

Risk Input Parameters (Emissions, Unit Risk Factors, Dipersion Data)

Emissions (Q) = 4.2 lb/yr (1.2E-02 lb/day) methylene chloride
= 2.3 lb/yr (6.E-03 lb/day) chloroform
X/Q = 3.633
Unit risk factors: 5.3E-06 (μg/m^3)$^{-1}$ chloroform, 1E-06 (μg/m^3)$^{-1}$ methylene chloride

Baseline Risk Screening Calculations

MICR = Q × X/Q × U × MP for VOC, MP = 1
MICR (methylene chloride) = (1.2E-02 lb/day) × 3.633 × (1E-06) = 4.4E-08
MICR (chloroform) = (6.3E-03 lb/day) × (3.633) × (5.3E-06) = 1.2E-07
Σ MICR = 1.6E-07 risk from secondary clarifier without controls

Total project risk (w/o controls) = (2.4E-07) + (1.8E-05) + (1.6E-07) = (1.8E-05) (Summing risks from each emission source)

Risk Screening Calculations (w/Controls)

No controls needed for secondary clarification

Guidance/Comments

This optional worksheet has been included to allow the user to calculate baseline risks (uncontrolled or current level of control) and risks after incorporating controls. The results of this risk screening can be added to Worksheets 2-2 and 4-1. One worksheet should be used for each new or modified source.

Risk Screening Methodology: This space has been provided to describe the methodology to be used in the risk screening analysis. For the example, a screening level similar to the South Coast Air Quality Management District (SCAQMD) Rule 1401 (New Source Review of Toxic Air Contaminants) has been used. This method requires the implementation of Toxic BACT or T-BACT if the maximum individual cancer risk from a project's new or modified sources (including cumulative impacts from other permitted units if permit applications were submitted on or after June 1, 1990) is greater than 1E-06. Once T-BACT has been installed, a risk of less than or equal to 10E-06 is required to meet the risk criteria and to obtain a permit. It is assumed for the example that only the risk from the three new emission sources contribute to the maximum individual cancer risk.

Pollutants: Methylene chloride and chloroform are considered in this example.

EXAMPLE NO. 2 WORKSHEET 2-3 (CONTINUED)
Optional Risk Screening

Risk Input Parameters: This space has been provided to list unit risk factors, uncontrolled emission rates and air dispersion data if needed. For the example, unit risk factors for methylene chloride and chloroform and the X/Q dispersion factor were obtained from the SCAQMD document entitled "Procedures for Preparing Risk Assessments to Comply with Air Toxics Rules of the South Coast Air Quality Management District, January 1992." This document provides the complete risk screening methodology used in the example. The uncontrolled source emission rates are also listed here (obtained from Worksheet 2-2).

Baseline Risk Screening Calculations: The equation used in the example was obtained in the above risk assessment guidance document. MICR is the maximum individual cancer risk, U is the unit risk factor, Q is the uncontrolled emission rate of the source, and MP is the multipathway adjustment factor. The maximum individual cancer risk was calculated for each pollutant and each source and summed by source and in turn by total project (i.e., all three sources in the example). MP for VOCs is 1 since a multipathway analysis is not typically needed for gaseous pollutants. Example results indicate that only risks from the diffused air activated sludge system exceed 1E-06. As a result, T-BACT would be required.

Risk Screening Calculations (w/Controls): This space is provided to document the risk reduction results from the installation of emission control technologies. In the example, two control options were analyzed for the diffused air activated sludge system: Control Option 1: Use of an atomized mist system assuming 70% of the emissions and risk would be reduced, and Control Option 2: Use of a recuperative thermal incinerator with 70% heat recovery assuming 90% of the emissions and risk would be reduced. Use of either control option would result in risks from the diffused air activated sludge system that are less than 10E-06, which meets SCAQMD Rule 1401 risk requirements. Only two control options were evaluated here to simplify the example. In practice, several control options may need to be evaluated.

The two control options can be carried forward in the analysis because they meet required risk criteria.

EXAMPLE NO. 2 WORKSHEET 3-1
Preliminary Control Technology — Evaluation and Rating*

Technologies	Source I.D. # 001	Source I.D. # 002	Source I.D. # 003	Source I.D. #	Source I.D. #
Air Stream Concentration	10-100 ppm	1-10 ppm	0-2 ppm		
Traditional Vapor Phase					
Thermal-No Heat Recovery	L1	L1	L1		
Thermal-Heat Recovery	L1	L1	L1		
Thermal-Catalytic	L1	L1	L1		
Activated Carbon	L1	L1	L1		
In situ Regenerative Activated Carbon	L1	L1	L1		
Non-Traditional Vapor Phase					
Soil Filters	U	U	U		
Process Air Recycle	U	U	U		
Atomized Mist	U	U	U		
Packed Towers	U	U	U		
Containment					
Passive	L1	L1	L1		
Vented/Occupied	L2	L2	L2		
Vented/Non-Occupied	L2	L2	L2		
Process and Practices					
Turbulence Reduction	U	U	U		
Operational Changes	U	U	U		
Wind Break	L1	L1	L1		
Process Substation	U	U	U		
Industrial Pretreatment	U	U	U		
Product Substitution	U	U	U		
Other Controls					

Guidance/Comments

Worksheet 3-1 should be completed as described in Example No. 1. The worksheet does not change from the first example.

* Assign control technology rating criteria codes (from Table 4.2.2) for each source and control option. If additional site-specific data are available, they should also be used in the evaluation.

EXAMPLE NO. 2 WORKSHEET 4-1
Feasibility Evaluation

Evaluation Criteria		Application Description		Expected Performance		Economic Impacts		Energy Impacts		Environmental Impacts		Feasibility Assessment Results	
Control Technology: Atomized Mist													
Application: Diffused Air Activated Sludge													
Pollutants	VOCs methylene chloride, chloroform	Air stream Concentration (ppm)	0–2	Emission Reduction	0.09 tpy methylene chloride, 0.1 tpy chloroform	Annualized Cost ($/yr)	1,000,000/yr Atomized Mist + 1,150,000/yr Cover = 2,150,000/yr	Fuel Type	—	Cross-Media Impacts Solid Waste	—	Technically feasible, unproven for VOC control, costs are high	Carry Forward ☐ Discard ☐
Cost Criteria ($/ton)	—	Air stream (cfm)	135,000	Percent Reduction	70%	Cost-Effectiveness ($/ton)	10.75 million/ton[a]	Fuel Consumption	—	Wastewater	Potential wastewater impact		
Performance Criteria (% reduction, tons reduced ppm, tons per year)	—	Uncontrolled Emissions (tpy)	0.13 methylene chloride, 0.14 chloroform	Controlled Emissions (tpy)	0.04 methylene chloride, 0.04 chloroform	Acceptable not applicable	Yes ☐ No ☐	Electric Demand	6.5 kWH/yr/cfm = 2.5 BTU/hr/cfm	Secondary Emissions	—		
Allowable Risk	10E-06 after controls (total project)	Acceptable (Figure 4-1)	Yes ☐ No ☐	Technical Limitations	Resolvable ☐ Unresolvable ☐			Acceptable	Yes ☐ No ☐	Toxic Emissions	Potential vapor chlorine leaving system		
Acceptable Energy Usage BTU/hr/cfm	2,762									Risk Screen Results (Optional)	5.5E-06		
										Acceptable	Yes ☐ No ☐		

EXAMPLE NO. 2 WORKSHEET 4-1 (CONTINUED)
Feasibility Evaluation

Evaluation Criteria		Application Description		Expected Performance		Economic Impacts		Energy Impacts		Environmental Impacts		Feasibility Assessment Results	
Control Technology: Recuperative Thermal Incineration (w/70% Heat Recovery)													
Application: Diffused Air Activated Sludge													
Pollutants	Methylene chloride, chloroform	Air stream Concentration (ppm)	0-2 ppm (VOC total)	Emission Reduction	0.12 tpy methylene chloride, 0.13 tpy chloroform	Annualized Cost ($/yr)	1,000,000/yr incinerator + 1,150,000/yr Cover = 4,650,.000/yr	Fuel Type	Natural Gas	Cross-Media Impacts Solid Waste	–	Technically feasible, potential heat exchanger fouling/corrosion, unproven for dilute streams such as this source. High cost.	Carry Forward ☐ Discard ☐
Cost Criteria ($/ton)	—	Air stream (cfm)	135,000	Percent Reduction	90%	Cost-Effectiveness ($/ton)	15 million/ton[a]	Fuel Consumption	0.015 scfm/yr/cfm	Wastewater	–		
Performance Criteria (% reduction, tons reduced ppm, tons per year)	–	Uncontrolled Emissions (tpy)	0.13 methylene chloride, 0.14 chloroform	Controlled Emissions (tpy)	0.01 methylene chloride, 0.01 chloroform	Acceptable not applicable	Yes ☐ No ☐	Electric Demand	23.8 kWH/yr/cfm	Secondary Emissions	0.14 lb/mmBTU (HC)[b], 0.37 lb/mmBTU CO, 0.068 lb/mmBTU NO_x		
Allowable Risk	10E-06 after controls (total project)	Acceptable (Figure 4-1)	Yes ☐ No ☐	Technical Limitations	Resolvable ☐ Unresolvable ☐			Acceptable	Yes ☐ No ☐	Toxic Emissions	Potential products on incomplete combustion		

Acceptable Energy Usage BTU/hr/cfm. This type of control is acceptable	This type of control is acceptable	Risk Screen Results (Optional)	1.8E-06
		Acceptable	Yes ☐ No ☐

Guidance/Comments

Separate copies of Worksheet 4-1 should be used for each control technology application that meets the previously agreed upon control technology acceptance criteria. To simplify the example, separate worksheets were prepared only for select control technologies that will subsequently be used in the control alternatives. If the given criteria listed in the worksheet is met or the user is not certain, then the “Yes” box should be checked. If the criteria is unacceptable, the “No” box should be checked.

Evaluation Criteria: The evaluation criteria specified in Worksheet 1-1 have been presented here as reference. The acceptable energy usage value presented in each worksheet (2762 Btu/hr/cfm) is based on the combined Btu output from fuel consumption and electric usage in an equivalently sized recuperative thermal incinerator without heat recovery. It is assumed that higher energy requirements in a control system are unacceptable. The risk criteria was taken from the SCAQMD Rule 1401 (New Source Review of Carcinogenic Air Contaminants).

Application Description: The VOC air stream concentration and uncontrolled methylene chloride and chloroform emission rates have been brought over from Worksheet 2-2. The emission rates have been converted from pounds to tons. To determine the VOC air stream rate (in cfm), it is assumed that 1 cfm of air is needed for each square foot of source cover. As a result, the air stream flow rate is equivalent to the total cover area. If the air stream characteristics do not meet the guidance provided in Figure 4.1, the “No” box should be checked. If the air stream characteristics do meet the guidance or if you are uncertain, then the “Yes “ box should be checked. In each case in the example, the air stream characteristics are acceptable for the corresponding control.

Expected Performance: The emission reduction and controlled emission rates were calculated based on typical percent control efficiencies for each control technology. These control efficiencies were obtained from the Control Technology Data Sheets (Section 4.4). In the case of add-on control equipment, the emission reductions and controlled emissions presented are for the add-on equipment alone. It was assumed that the covers and vents alone would not reduce highly volatile emissions such as methylene chloride and chloroform. The preliminary assessment indicated that any technical limitations are resolvable and, as a result, the “Resolvable” box was checked for each control technology application.

Economic Impacts: Although economic impacts may not need to be determined in an incremental emission (risk) reduction process, they are calculated here to help select the least costly control alternative. Annualized costs for the atomized mist and recuperative thermal incineration (with 70% heat recovery) systems were determined directly from cost curves provided in the Control Technology Data Sheets (Section 4.4). By knowing the required air flow, one can directly read the annualized cost of control.

Annualized costs for nonoccupied covers and vents were based on the equations in the Control Technology Data Sheet for this technology (Section 4.4.3.3). The annualized cost calculation assumes a capital recovery factor of 16.28% (typically used in the control cost data sheets provided in Appendix B) and an annual maintenance cost equivalent to 5% of the total purchased cost. The annualized cost for the add-on control devices included the annualized cost for covers and vents.

Cost effectiveness was determined by dividing the total annualized cost of control by the tons of emissions reduced. For this example, cost-effectiveness is only used as a comparison tool to select this least-cost alternative that meets the acceptable risk criteria.

EXAMPLE NO. 2 WORKSHEET 4-1 (CONTINUED)

Feasibility Evaluation

Feasibility Assessment Results: The summary of each control technology feasibility assessment is included here. Pertinent control technology data sheet information on typical performance, applicability and assessment of current knowledge should also be summarized here. For the example, the two control options meet the risk criteria as stated in SCAQMD Rule 1401. As a result, these options have been carried forward in the analysis.

Environmental Impacts: Qualitative information relative to environmental impacts are summarized in the Control Technology Data Sheets (Section 4.4). This and any other site-specific information should be summarized on the worksheet. For the example, pertinent environmental impacts from the data sheets are summarized in each worksheet. It is uncertain at this stage whether there is a significant or adverse environmental impact for the example. As a result, the “Yes “ box was checked for each application of each control technology.

Energy Impacts: Energy data are also provided in the example to allow an energy usage comparison between each control option. This could assist in the final control technology selection process. Fuel consumption and energy demand data were obtained from the Control Technology Data Sheets (Section 4.4).

[a] \$ per combined ton of methylene chloride and chloroform removed.

[b] HC = hydrocarbons.

EXAMPLE NO. 2 WORKSHEET 5-1
Control Alternative Development

Alternative No.	Strategy Description	Initial Assessment
1	Uncovered primary sedimentation, diffused air activated sludge with atomized mist, uncovered secondary clarifier	Potential wastewater impact and vapor chlorine leaving diffused air system, technically feasible, unproven for VOC control, high cost
2	Uncovered primary sedimentation, diffused air activated sludge with recuperative thermal incineration (70% heat recovery), uncovered secondary clarifier	Potential heat exchanger fouling/corrosion, unproven for diluting streams, technically feasible, high cost

Guidance/Comments

Control alternatives were developed for the three emission sources. Control systems were required only for the diffused air activated sludge system. A description of these alternatives is provided in this worksheet as well as a summary of the feasibility evaluation information from Worksheet 4-1.

EXAMPLE NO. 2 WORKSHEET 6-2
Alternative Comparison

	Performance			Preliminary Cost Data[b]				
Control Alternative[a]	Emission Reduction Potential (tpy)	Control Level (%)	Controlled Emissions (tpy)	Annualized Cost ($/yr)	Cost-Effectiveness ($/ton)	Risk Level[c]	Regulatory Acceptance Criteria[d]	Preliminary Assessment Comments
1	0.09 methylene chloride 0.1 chloroform	70 (diffused air)	0.04 methylene chloride 0.05 chlorofrm	2,150,000	10.75 million/combined ton*	6E-06	10E-06 project risk	Meets risk criteria, lower cost than Alt. 2; select this alternative.
2	0.12 methylene chloride 0.13 chloroform	90 (incineration)	0.02 methylene chloride 0.02 chloroform	4,650,000	15 million/combined ton*	2E-06	10E-06 project risk	Meets risk criteria, higher cost than Alt. 1.

Guidance/Comments

The emission reduction potential and controlled emissions presented in this worksheet were calculated for the two control alternatives by summing the individual control technology emission data from Worksheet 4-1. The control cost data presented in this worksheet were also summarized from individual control technology cost data calculated in Worksheet 4-1. For the example, the cost data were used only to rank each alternative according to cost. Since the two control alternatives met the required risk criteria and have been determined to be technically feasible, the atomized mist alternative was preliminarily selected since it was the least-cost alternative. A detailed control alternative analysis (Worksheets 6-1 and 6-2) may be needed to fine tune the cost of control to ensure that there are no significant or adverse environmental impacts associated with the preliminarily selected control alternative. The other control alternatives evaluated in Worksheet 5-1 may also be carried forward to the detailed analysis phase to ensure that the appropriate control alternative has been selected.

[a] If top down BACT process is used, rank each alternative according to control effectiveness, with the highest control effectiveness alternative on the top of worksheet. If the incremental emission reduction procedure is used, rank each alternative according to cost effectiveness, with the most cost-effective alternative at the top of worksheet.

[b] Generalized cost data obtained from Worksheet 4-1 (Technical Data Sheets in Section 4.4).

[c] Risk level may be risk prioritization score, risk screening level, or refined risk assessment level.

[d] Regulatory acceptance criteria may be cost effectiveness, required emissions or risk reduction level, or allowable project emission or risk level.

* Combined ton is sum of methylene chloride and chloroform reduced.

APPENDIX III

WORKSHEET

AUDITING TABLE FOR DETERMINING AIR QUALITY PROGRAM ELEMENTS BY TASKS AND FUNCTIONAL ORGANIZATIONAL UNITS (FTE/MGD)

1566768209/03/$0.00+$1.50
© 2003 by CRC Press LLC

WORKSHEET

Program Element	Operations	Maintenance	Planning and Design Engineering	Administration	Source Control	CIP Engineering	Construction Management	Process Engineering	Internal Auditors	Research Projects	Total
Process Monitoring and Control											
Daily, weekly, monthly, and annual sampling											
Abatement equipment checks											
Calibrate and span monitors											
Document chemical/fuel usage											
Recordkeeping and reporting											
Collect compliance data											
Format/update compliance database											
QA/QC database											
Maintain database											
Provide compliance data and reports											
Preventive and corrective maintenance											
Conduct PM per equipment specifications											
Conduct CM, as needed											
Target compliance equipment for highest CM and PM activities											
QA/QC any PM or CM											
Maintain monitoring systems and equipment											

Regulatory interactions and odor compliant responses											
Handle regulatory tours and information requests											
Follow-up with regulatory agencies											
Track new, pending, or modified AQ laws and regulations that impact POTWs											
Develop and implement odor complaint phone and response program											
Conduct perimeter odor survey and measurements											
Implement response program and follow-up											
Document and track regulatory requests and odor complaints											
Compliance investigation and follow-up											
Investigate regulatory issues or odor complaints											
Develop responses and issue											
Take corrective actions on policy, equipment, or practice based on investigation											
QA/QC investigations and tools used											
Provide both written and verbal responses											

WORKSHEET (CONTINUED)

Program Element	Operations	Maintenance	Planning and Design Engineering	Administration	Source Control	CIP Engineering	Construction Management	Process Engineering	Internal Auditors	Research Projects	Total
Process optimization Conduct optimization sampling and process investigations Adjust process and abatement equipment set points Identify Process compliance problem areas and implement correction program Communicate with O&M on optimization changes Implement process optimization changes, policies, practices or equipment											
Research, special studies, troubleshooting and emissions characterization Conduct, as Needed, research and special studies to characterize air emissions and viable abatement approaches											

Review CIP projected projects and process optimization activities for research or innovative abatement needs or approaches											
Track current and pending abatement equipment, compliance monitoring devices that can be viable to the POTW											
Planning, design and construction											
Determine air quality permitting needs and compliance trigger levels/requirements											
Attain air quality permits											
Include air quality monitoring, abatement needs and compliance databases into planning and design											
Ensure abatement equipment is installed correctly											
Turnover Abatement equipment needs and operational requirements to O&M											
Administration activities											
Budget for air quality compliance needs – capital, chemical and staffing											
Budget for O&M air quality compliance needs											

WORKSHEET (CONTINUED)

Program Element	Operations	Maintenance	Planning and Design Engineering	Administration	Source Control	CIP Engineering	Construction Management	Process Engineering	Internal Auditors	Research Projects	Total
Implement POTW's air quality compliance policy and track compliance in organization											
QA/QC compliance documentation and correspondence with regulatory agencies											
Provide air quality related training and safety awareness											
Budget for air quality permit renewal costs											
Subtotals											
Grand total =											

Index

A

Acetaldehyde, 207
Acrolein, 207
Acrylonitrile, 38
Activated sludge system(s), 80
  factors affecting emissions for, 81
  pure-oxygen, 287
  volatilization in, 148
Aerated grit chamber(s), 118
  comparison of PEEP and Canadian study emission factors for, 258
  emission(s)
    factors derived from, 231
    origination of, 78
Aeration
  basins, ventilation rates for covered, 290
  bubble, 82
  diffusers, 80
  high-purity oxygen, 245
  rates, minimizing of, 290
  subsurface diffused, 245
  system, sorption in, 152
  tank(s)
    biodegradation losses of VOCs in, 151
    compositing of air samples collected from, 204
    step-feed, 279
Aerobic biological treatment processes, 60
Aerobic digestion, 62, 87, 88
Afterburners, 292, 296
Air
  dispersion modeling, 1
  emission(s)
    characteristics of from POTWs, 320
    controls, evaluation of, 323
    DAF, 137
    speciations, wastewater facility payment for, 63
  exchange rates, 107
  flow regimes, co-current, 161
  –wastewater interface, drag force at, 76
Air quality
  ambient monitoring of existing, 13
  assessment, responsibilities for, 355
  compliance
    assessment, 342
    barriers preventing optimized, 2
    BMPs for, 338
    strategy, 5, 37
  management
    district (AQMD), 220
    plans (AQMPs), 321
  permits, 346, 357
  policy, development of written, 355
  program elements, auditing table for determining, 395–400
  regulations, *see* U.S. air quality regulations
Air quality compliance program(s)
  case study, 347–357
    good-neighbor actions, 355–356
    incident command system, 357
    responsibilities for air quality assessment, prevention, response and control, 355
    supporting POTW ECHO, 356–357
  critical mass, 354
  development of, 338
  efforts, BMPs of, 348–353
  elements, 344–347
    administrative activities, 346
    compliance investigation and follow-up, 345
    correlating best management practices, 347
    determining general FTE requirements, 346
    planning, design and construction, 346
    preventive and corrective maintenance, 345
    process monitoring and control, 344
    process optimization, 345
    recordkeeping and reporting, 345
    regulatory interactions and odor complaint response, 345
    research, special studies, troubleshooting and emissions characterization, 346
  fine tuning of, 361
  requirements of best, 1
Air sample(s)
  analysis for HAPs in, 205
  compositing of, 204
  detection of TAC in, 221

Air toxic(s)
  assessment of, 34
  compound list, AMSA recommended, 70–71
  control of from urban fugitive sources, 319
  undetected, 219
Aldehydes, 210
Alkanes, 41
ALOHA model, *see* Area locations of hazardous atmospheres model
Alternate test procedures (ATPs), 222
Ambient air quality deterioration, 12
American Petroleum Institute (API), 164
AMSA, *see* Association of Metropolitan Sewerage Agencies
Anaerobic digestion, 62, 87, 88, 232
Analysis of variance (ANOVA), 137, 165
Anilines, 210
ANOVA, *see* Analysis of variance
API, *see* American Petroleum Institute
Appurtenances, 60
AQMD, *see* Air quality management district
AQMPs, *see* Air quality management plans
Area locations of hazardous atmospheres (ALOHA) model, 29
Aromatic nitro compounds, 210
Association of Metropolitan Sewerage Agencies (AMSA), 47
ATAD, *see* Auto-thermophilic aerobic digesters
ATPs, *see* Alternate test procedures
Auto-thermophilic aerobic digesters (ATAD), 139

B

BACT, *see* Best available control technology
Bacteria, biodegradable contaminants as food for, 312
BAFs, *see* Biological aerated filters
Baked out organic matter, 299
Barometric pressure
  gradient, 76
  ventilation and, 107
Bar racks, emissions from, 117
BASTE model, *see* Bay Area Sewage Toxics Emission model
Bay Area Sewage Toxics Emission (BASTE) model, 3, 91, 122, 145, 151, 240, 272
Belt filter press(es)
  refinery sludge treatment by, 176
  schematic of, 173
  sludge dewatering, 87, 238, 259
  VOCs volatilized in, 172
Benzene, toluene and xylenes (BTXs), 41
Best available control technology (BACT), 5, 13, 286, 320
  Clearinghouse data, 332
  determination, POTW, 63
Best Management Practices (BMPs), 346, 347, 348–353
Biodegradable compounds, biofilter treatment of, 312
Biodegradation, 149
  constants, 246
  mass flux due to, 163
  model predictions of, 160
  rate coefficients, 160, 169
Biofilm
  conceptual schematic of, 158
  model, 169
  process model, 157
  removal of VOC in, 157
  thickness, 158
Biofilter(s)
  compost, 311
  configurations, types of, 308
  costs, 313
  efficiency, 312
  in-ground, 308, 309
  media, 310
  performance, 315
  removal efficiencies of, 311
  use of for odor control, 313
  VOC removal efficiency of, 314
Biofiltration, 5, 307
Biological aerated filters (BAFs), 155
Biological tower systems, 81
Biological treatment systems, VOC emissions from, 145–153
  fate of VOCs in biological treatment, 147–152
    sorption, 148–152
    volatilization and stripping, 147–148
  process description, 146–147
    activated sludge process with diffused aeration using air, 146
    activated sludge process using high purity oxygen, 146
    mechanical aeration processes, 146–147
Biological wastewater treatment systems, 61–62
  attached media reactors, 62
  diffused air activated sludge, 61
  high purity oxygen activated sludge, 62
  mechanically aerated activated sludge, 62
Bioreactors, trickle-bed, 307
Bioscrubbers, 307, 312
Biosolid(s)
  dewatering processes, VOC emissions from, 171–188
  incinerators, 89, 94, 293

  VOCs associated with, 90
Biotrickling filter(s)
  disadvantages of, 312
  performance of, 310
BMPs, *see* Best Management Practices
Boilers, 62, 89
  emission factors derived from, 232
  factors affecting emissions from, 93
BTXs, *see* Benzene, toluene and xylenes
Bubble aeration, 82
Buoyancy, ventilation and, 107

C

CAAAs, *see* Clean Air Act Amendments
California Air Toxics Emission Factors (CATEF) tables, 215
Canister sampling, 195, 196
Capital improvement plan (CIP), 346
CAPs, *see* Clean air plans
CARB Method 429, 212, 213
Carbon
  adsorption, 5, 60, 305, 308
  monoxide, 90
  scrubbers
    advantages of, 306
    disadvantages of, 306
  tetrachloride, 38
CAS, *see* Chemical Abstracts Service
Catalytic incinerators, 5
  availability of, 300
  uses of 300
  VOCs destroyed by, 299
CATEF tables, *see* California Air Toxics Emission Factors tables
Centrifuge(s)
  emission factors derived from, 233
  emissions from full-scale, 180
  foul air from, 180
  mass balance for solids around, 181
  operation of, 172
  outputs, distribution of representative VOCs in, 183
  process streams
    flow and suspended solids concentrations in, 182
    mean concentrations of VOCs in, 182
  schematic of, 173
  Sharples, 180
Chemical Abstracts Service (CAS), 244
Chlorinated compounds, emission rates of, 279
Chlorinated hydrocarbons, emission rates of, 66
Chlorination, 62, 237, 259
Chlorine
  contact tank, emission factors derived from, 231
  disinfection, THMs formed during, 84
Chloroform, 38, 66
Chromatographic columns, maintenance of, 217–218
Chromic acid anodizing, 36
Chromium electroplating, 36
CIP, *see* Capital improvement plan
Clarifier(s)
  reduced number of, 291
  secondary, 262, 279
  surface, emissions from, 119
  weirs, emissions at, 123
Clean Air Act, 12
Clean Air Act Amendments (CAAAs), 2, 8
  air toxics list, 19–23
  provisions of, 9
  Title III list, 67
Clean air plans (CAPs), 321
Clean Water Act NPDES program, 30
Collection system(s)
  components, 75
  emission of VOCs from, 75, 95
  estimation of VOC emissions by, 229
  models, 240–243
    BASTE model, 240
    CORAL model, 240, 241
    naUTilus model, 240, 243
    TOXCHEM model, 240, 242
    WATER8 model, 240, 242
    WATER9 model, 240, 242
  types of, 60, 340
Combined sewer area overflows, runoff from, 340
Combustion
  devices
    airflow rate to, 234
    mass loading of pollutant to, 234
  exhaust gases, 292
  process(es), 88–90
    boilers, 89
    emission mechanisms for, 90
    factors affecting emissions for, 91
    flares, 89
    incinerators, 89–90
    internal combustion engines, 89
    pollutants emitted from, 88
  sources
    boilers, 62
    flares, 62
    incinerators, 62
    internal combustion engines, 62
    sampling of, 200
Commercial sterilization facilities, 36

Community health risks, initiatives to identify, 34
Compliance
  audit, 27
  data compiling, 345
  documentation, 343
  investigation, 345
Compost biofilters, 311
Comprehensive fate models, performance evaluation of, 267
Conservative mass balance, estimation of VOC emissions by, 229
Containing processes, 287
Continuous stirred tank reactor (CSTR), 163
Control technologies, 285–318
  comparison of, 291–314
    biofiltration, 307–314
    carbon adsorption, 305–306
    catalytic incinerators, 299–300
    dry chemical scrubbing, 305
    flares, 293–295
    incinerators, 293
    mist scrubbers, 303–305
    packed-tower scrubbers, 302–303
    recuperative oxidizers, 295–297
    regenerative oxidizers, 297–299
    thermal treatment, 291–293
    wet scrubbing, 300–301
  control alternatives, 332
  cost effectiveness, 331
  elimination of infeasible, 329
  energy impact analysis, 332
  overview, 286–291
    containment, 287–290
    nontraditional vapor phase controls, 287
    process and practice modifications, 290–291
    source control, 291
    traditional vapor phase controls, 286
  process requirements, 326
  rating of potential, 329
  regulatory acceptance criteria, 332
Control technology evaluation, 319–334
  detailed control technology evaluation methodology, 324–333
    definition of process requirements, 326–328
    development of alternatives, 331
    elimination of infeasible technologies, 329–331
    evaluation of most effective control alternatives, 332–333
    identification of applicable emission sources, 328–329
    rating of potential control technologies, 329
  incremental emission reduction procedure, 333
  overview of existing control technology evaluation processes, 320–324
    incremental emission reduction procedure, 322–324
    top-down BACT procedure, 321–322
CORAL model, 112, 240, 241
Corrosive compounds, formulation of, 297
Covering system erosion rates, 290
Cremation, 36
Cross-flow scrubbers, 302
Cryogenic trapping, HAPs analysis by, 207
CSTR, *see* Continuous stirred tank reactor
Cyclohexanes, 41

D

DAF, *see* Dissolved air flotation
Dechlorination facilities, emission factors derived from, 232
Deficit ratios, 106
DEGADIS computer dispersion model, *see* Dense gas dispersion computer dispersion model
Degreasing operations, discharges from, 339
Denitrification filtration, 60
Dense gas dispersion (DEGADIS) computer dispersion model, 29
Depressed sewers, 75
Design Institute for Physical Properties (DIPPR) 911 database, 244
Detection limit, most common definition of, 218
Detritus tanks, 119
Dewatering, 62
  belt press, 87, 88
  processes, linear regression parameters for emissions from, 186
    concentrations of VOCs in air exhausted, 176
    Henry's law coefficient for, 184
    VOC emission from, 339
    VOC transfer in, 172
Diffused air activated sludge, 237, 259, 262
  comparison of PEEP and Environment Canada emission factors for, 257
  process, 234
Digester gas, 28
  BTXs in, 41
  burning of excess, 293
  incomplete combustion of, 41
  sulfides in, 90
  VOC emissions, 237
2,4-Dinitrophenylhydrazine (DNPH), 214

Dioxins, 207
DIPPR 911 database, *see* Design Institute for Physical Properties 911 database
Disinfection, 60, 83
  alternatives to chlorine for, 291
  chlorine, formation of trihalomethanes during, 84
Dissolved air flotation (DAF), 85, 127, 237, 259
  air emissions from, 137
  flow schematic, pilot, 132
  pilot plant, 131
  process, bubbles generated in, 129
  thickening, 85, 232
  unit(s)
    comparison of predicted and observed emissions rates, 139
    measuring emissions from, 128
    schematic of, 128
  VOCs stripped in full-scale, 142
  volatilization from by mechanism, 140
Dissolved air flotation, VOC emissions from, 127–143
  measuring emissions from DAF units, 128
  modeling, 129–131
  pilot and field studies, 131–141
    full-scale studies, 141
    pilot studies, 131–141
  process description, 127–128
Dissolved oxygen
  concentration, 102
  control, automatic, 290
DNPH, *see*2,4-Dinitrophenylhydrazine
DOS-based model, 244
Dosed water testing, 140
Drop shafts, 75
Dry chemical scrubbing, 5, 305
Dry cleaning facilities, 36

E

EBMUD, 202
EF, *see* Emission factors
Effluent
  filtration, 62, 82, 263
  recycle, 137, 165, 308
ELCD, *see* Electrolytic capture detector
Electrolytic capture detector (ELCD), 194
Electroplating industry, discharges from, 339
Elevated flares, 294
Emergency response program, 28
Emission(s)
  cause of, 117
  control(s), 4–5
    nontraditional, 324
    pollutants requiring, 328
  DAF, 142
  dewatering process, 186
  estimation, potential approaches to, 4–5
  factors (EF), 93, 94, 235
    BACT/LEAR model, 240
    computing of, 238
    concentration-based, 229, 230
    derivation of, 174, 249
    flow-related, 229
    liquid process, 233
    PEEP, 223, 255
    TriTAC, 239, 260
    U.S. EPA AP-42, 240
    ways to derive concentration-based, 4
  hydrocarbon, 66, 90
  inventory, facility-wise, 31
  key factors affecting, 74
  measurement of, 74
  mechanisms, 74
  monitoring, purpose of, 222
  rate(s)
    lowest achievable, 15
    PSD applicability, 14
  reduction, 15
    best system of, 17
    potential, 324
    procedure, incremental, 322, 331, 333
  sources, risk screening analysis of, 323, 333
  toxic air contaminant, 220
  trickling filter, 81
Enclosed solids handling processes, 85
EPA, *see* United States Environmental Protection Agency
Estimation methods, VOC emission, 227–252
  concentration-based emission factors, 230–239
    Joint Emissions Inventory Program emission factors, 237–239
    Pooled Emission Estimates Program factors, 230–237
    TriTAC emission factors, 239
  conservative mass balance, 229
  flow-related emission factors, 229–230
  general fate models, 239–247
    collection systems, 240–243
    wastewater treatment systems, 243–247
  source testing, 247–248
    confined sources, 247–248
    unconfined sources, 248
  tracer method, 248–249
Ethers, 210
Ethylene dichloride, 38
Exhaust gases, calculation of emissions load in, 234

Explosives industry, discharges from, 339
Exponential model, 187

F

FATE model, *see* Fate and Treatability Estimator model
Fate and Treatability Estimator (FATE) model, 247
Federally enforceable state operating permits (FESOPs), 32, 347
Feed sludge sample, collection of, 180
FESOPs, *see* Federally enforceable state operating permits
FID, *see* Flame ionization detector
Filter(s), *see also* Trickling filter
  biotrickling, 310, 312
  effluent, 83
  gravity, 83
  press, mean concentrations of VOCs in, 179
Final effluent
  evaporation ponds, 237
  weir, 237, 259
Fish and Wildlife Service, 14
Fixed film processes, VOC emissions from, 155–170
  modeling, 156–169
    pilot scale studies, 163–169
    rotating biological contactor studies, 162–163
    trickling filters, 156–162
  process descriptions, 155–156
    rotating biological contactors, 156
    trickling filters, 155–156
Flame ionization detector (FID), 194
Flare(s), 5, 62, 89
  costs of, 295
  disadvantage with, 294
  elevated, 294
  factors affecting emissions from, 93
  ground level, 294, 295
  kinds of, 294
  performance, 294
  uses of, 293
  VOC destruction efficiencies of, 295
Float streams, analysis of VOCs in, 128
Flow equalization, 237, 259, 261
Fluidized bed incinerators, 89, 293
Flux chamber
  operation of, 196–197
  performance of, 199
  technology, 197
Formaldehyde, 207
Foul-air-stream flow rates, 299
Fourier Transform Infrared Method, Method CARB 430 vs., 214
Fourier transition infrared spectrophotometer (FTIR), 200
Froude number, 101
FTEs, *see* Full-time equivalents
FTIR, *see* Fourier transition infrared spectrophotometer
Full-time equivalents (FTEs), 5, 342, 343, 360
  critical mass air quality compliance program, 354
  requirements, 346
  spending of for air quality compliance program, 344

G

GAC, *see* Granular activated carbon
GACT, *see* Generally available control technology
Gas(es)
  chromatography (GC), 194
  digester, VOC emissions, 237
  exhaust, calculation of emissions load in, 234
  landfill migration, 208
  –liquid mass transfer, 76, 99, 155, 306
  to liquid ratio, 81
  phase mass transfer coefficient, 100, 150
  –solid mass transfer, 306
  soluble waste, 307
  velocity ratios, predicted-to-observed, 108
Gasoline
  distribution, 36
  vapors, 313
Gas Research Institute (GRI), 215
GC, *see* Gas chromatography
GC/MS
  analysis, purge-and-trap, 209
  data, evaluation of raw, 210
  determination of PAH by high-resolution, 212
  methods, sensitivity of, 205
  system, VOCs desorbed into, 206
General fate models
  collection systems, 240–243
  current generation of, 91
  estimation of VOC emissions by, 229
  VOC emissions from POTWs by, 260
  wastewater treatment systems, 243–247
Generally available control technology (GACT)
Geographic Information Systems (GIS) technology, 243
GIS technology, *see* Geographic Information Systems technology
Glass manufacturing, discharges from, 339
Good-neighbor actions, 355, 356

Grab samples, 192
Granular activated carbon (GAC), 305, 310, 313
Gravity
  filtration, 83, 237, 259
  thickening, 86, 232
GRI, *see* Gas Research Institute
Grit
  chamber(s)
    aerated, 118
    classification of, 118
    detritus tank, 118
    emissions from non-aerated, 78
    Stickney aerated, 277
    velocity controlled, 118
    VOC emission rates for, 269
    vortex-type, 118, 119
  removal, 261
Ground level flares, 294, 295

H

Haloethers, 210
Halogenated solvent cleaners, 36
HAPs, *see* Hazardous air pollutants
Hazard assessment/offsite consequence analysis, 27
Hazard and operability (HazOp) study, 30
Hazardous air pollutants (HAPs), 3, 8
  analysis for in air samples, 205
  emissions
    estimation of volatile, 111, 112
    predicted, 112
    total, 266
    U.S. EPA and, 221
  fugitive emissions of, 30
  instrumental analysis methods, 207
  list of for Integrated Urban Toxics Strategy, 35
  measurements, 265
  organic, subject to wastewater provisions of SOCMI HON, 68–69
  quantitation of, 191
  regulated, 31
  sampling procedures for, 193
  volatile organic, 194
Hazardous air pollutants, sampling and analytical methods for, 189–225
  analytical methodology, 205–216
    CARB Method 429, 212–214
    CARB Method 430, 214–216
    SW-846 Method 8260 B, 208–209
    SW-846 Method 8270 C, 210–211
    SW-846 Method 8280 A, 211–212
    U.S. EPA Method 18, 208
    U.S. EPA Method 25 C, 209–210
    U.S. EPA Method TO-14, 206–208
  analytical procedures and calibration frequencies, 217–218
    analytical procedures, 217
    analytical quality control samples, 218
    calibration procedure and frequency, 217–218
    laboratory standards, specialty gases and reagents, 217
  method detection limits and reporting levels, 218–221
    achieving lower MDLs in various matrices, 218–219
    guidelines for reporting data below detection levels for risk management and potential health risk assessments, 219–221
  perspective and connectivity, 221–223
    traditional and performance-based regulatory compliance monitoring, 222–223
    use of direct assessment techniques for risk assessment, 221–222
  quality assurance, 216–217
    field blanks and duplicates, 217
    representatives, 216
    sample chain-of-custody, 216–217
    sample integrity, 216
  sampling methodology, 191–205
    compositing of air samples, 204–205
    compositing methodology for liquid VIC samples, 202–204
    liquid sampling, 192
    sampling for ambient air and non-combustion point sources, 192–200
    sampling of combustion sources, 200–202
    solids sampling, 192
Hazardous Organic NESHAP (HON), 67
Hazardous waste combustors, 36
HazOp study, *see* Hazard and operability study
Headspace
  velocities, 111
  ventilation rate, 105, 107
Health risk assessments (HRAs), 219
Heat
  exchanger, 292, 296
  recovery systems, 292
Henry's Law coefficient(s), 65, 129, 160, 184, 246
  compound estimates based on, 66
  percent volatilized vs., 136
  relationship between percent volatilized and, 135
  temperature correction of, 149
  VOC volatilization losses and, 76
  wastewater temperature and, 99

Henry's law constant(s), 100, 107, 148
  ability of BASTE model to correct, 152
  dimensionless, 120
  high, 79
  oxygen, 103
  stripping efficiencies and, 104
  temperature correction for, 150
  VOC, 103
Herbicides, 207
High purity oxygen (HPO), 80, 146, 290
  activated sludge, 62, 80
  aeration, 245
  systems, venting rate in, 81
HON, *see* Hazardous Organic NESHAP
Hospital sterilizers, 36
Hot Spots Information and Assessment Act of 1987, California Air Toxics, 191, 219
HPO, *see* High purity oxygen
HRAs, *see* Health risk assessments
Hydrocarbon(s), 92
  chlorinated, emission rates of, 66
  emissions, 66, 90
  photoreactives, 63
  total, 67

I

ICCR program, *see* U.S. EPA Industrial Combustion Coordinated Rulemaking program
ICE, *see* Internal combustion engine
Incinerator(s), 5, 62
  biosolids, 89, 293
  catalytic
    availability of, 300
    uses of, 300
    VOCs destroyed by, 299
  emissions, 18, 32
  fluidized bed, 89, 293
  recuperative, 297
  VOC emission from, 87
  zones, 89
Incremental emission reduction procedure, 322, 331, 333, 381–394
Industrial boilers, 36
Industrial discharges, 105, 339
Industrial pretreatment programs, enforcement of, 291
Industrial process drains, ventilation rates from, 111
Influent feed systems, turbulence of, 291
Ingersoll filter press
  distribution of VOCs exiting, 181
  mass balance of VOCs around, 179
  observed and estimated emissions from, 185
  process stream characterization, 178
In-ground biofilter, 308, 309
Inorganic chemical manufacturing, industrial, 36
Inside the battery limit (ISBL), 243
Institutional/commercial boilers, 36
Instrument calibration protocols, 217
Integrated Urban Strategy, 33, 35
Interceptor sewers, 75
Internal combustion engine (ICE), 62, 89, 215
  emission factors derived from, 232
  factors affecting emissions from, 92
  stationary, 36
Inverted siphons, 75
ISBL, *see* Inside the battery limit

J

JEIP, *see* Joint Emissions Inventory Program
Jet fuel, 313
Joint Emissions Inventory Program (JEIP), 3, 60, 71
  emission factors, 237, 254, 255
  factors, estimation of VOC emissions by, 229
  study, emission factors for unit processes in, 259

K

Ketones, 210

L

Laboratory instruments, calibration of, 217
LAER, *see* Lowest achievable emission rate
Lagooning, 62
Landfill(s)
  measurement of nonmethane organic compounds from, 209
  migration gas, 208
Lateral sewers, 75
Lean burning engines, 89, 215
LEL, *see* Lower explosive limit
Liquid
  drag, ventilation and, 107
  –gas mass transfer, 166
  -phase mass transfer coefficient, 100, 102
  process(es)
    emission factors, 233
    uncovered, 233
  sampling, 192
  –solid partitioning, 131

Lower explosive limit (LEL), 297
Lowest achievable emission rate (LAER), 15, 320

M

MACT, *see* Maximum achievable control technology
Mass spectrometry (MS), 194
Mass transfer
  coefficient
    gas-phase, 100, 150
    liquid-phase, 100, 102
    oxygen, 125
  factors influencing rate of, 99
  gas–liquid, 76, 99, 155, 306
  gas–solid, 306
  liquid–gas, 166
  parameter, VOC substrate, 162
Material inventory, decrease of, 28
Maximum achievable control technology (MACT), 2, 18, 320
Maximum exposed individual (MEI), 25
MDLs, *see* Method detection limits
Mechanical activated sludge, 237, 259
Mechanical aeration, 262
Mechanical stripping rate, 150
Mechanical surface aeration, 148
Medical waste incinerators, 36
MEI, *see* Maximum exposed individual
Mercury cell chlor-alkali plants, 36
Method detection limits (MDLs), 206, 218, 219
Methylene chloride, 38, 66
Mist scrubbers, 5, 303, 304
Mixed liquor suspended solids (MLSS), 146
MLSS, *see* Mixed liquor suspended solids
Model(s)
  air dispersion, 1
  area locations of hazardous atmospheres, 29
  BASTE, 3, 91, 122, 145, 151, 240, 272
  Bay Area Sewage Toxics Emission, 91
  biofilm, 157, 169
  chlorinated VOC emissions predicted with, 281
  collection systems, 240–243
  compounds, properties of, 133
  comprehensive fate, performance evaluation of, 267
  computer dispersion, 29
  conservative nature of, 280
  CORAL, 112, 240, 241
  DOS-based, 244
  exponential, 187
  frequently used, 94
  general fate
    collection systems, 240–243
    estimation of VOC emissions by, 229
    VOC emissions from POTWs by, 260
    wastewater treatment systems, 243–247
  Nappe, 106, 108, 109
  naUTilus, 113, 240, 243
  non-chlorinated VOC emissions predicted with, 282
  noncomprehensive fate, performance evaluation of, 267
  pool, 106
  predictions
    biodegradation, 160
    volatilization, 160
  proprietary, VOC emissions estimated using, 239
  SEAM, 243
  surface volatilization, 139
  total VOC emissions predicted with, 281
  TOXCHEM, 3, 91, 147, 240, 264, 274
  TOXCHEM+, 94, 113, 123, 145, 153
  U.S. EPA
    Fate and Treatability Estimator model, 247
    public domain, 3
  WATER7, 269, 276
  WATER8, 91, 121, 145, 240, 279
  WATER9, 91, 94, 113, 125, 240
  weir, 124
  Windows-based, 244
Monod half-saturation constant, 161
Monod kinetics, 245
MS, *see* Mass spectrometry
Multiple hearth furnaces, 293
Municipal landfills, 36
Municipal waste combustors, 36
Municipal wastewater collection systems, mass discharges of VOCs to, 98

N

NAAQS, *see* National ambient air quality standards
Nappe model, 106, 108, 109
National ambient air quality standards (NAAQS), 8, 10
  ozone, 11
  proposed changes to, 11
National Emission Standards for Hazardous Air Pollutants (NESHAPs), 3, 8, 18, 67
National Fire Protection Association, 290
National Park Service, 14
Natural gas production, 36
naUTilus model, 113, 240, 243

NESHAPs, *see* National Emission Standards for Hazardous Air Pollutants
New source performance standards (NSPS), 3, 8, 15, 17
New York City Department of Environmental Protection (NYCDEP), 49, 50, 280
Nitrification, 60
Nitrophenols, 210
Nitrosamines, 210
NMOC, *see* Nonmethane organic compounds
Non-combustion point sources, sampling for, 192
Noncomprehensive fate models, performance evaluation of, 267
Nonmethane organic compounds (NMOC), 209
NSPS, *see* New source performance standards
NTCDEP, *see* New York City Department of Environmental Protection
Nucleoids, 127

O

OAQPS, *see* U.S. EPA Office of Air Quality Planning and Standards
Occupational Safety and Health Administration (OSHA), 25
Occupational Safety and Health Administration Process Safety Management (PSM), 25, 26, 28
Octanol-water partitioning coefficient, 130
Odor
  complaint response, 345
  control
    biolfilters used for, 313
    VOC emissions control and, 340
Oil
  refinery wastewater, 139
  –water separators, 245
Open burning scrap tires, 36
Organic chemical manufacturing, industrial, 36
Organic matter, baked out, 299
Organics, decomposition of, 86
Organophosphate esters, 210
OSBL, *see* Outside the battery limit
OSHA, *see* Occupational Safety and Health Administration
Outside the battery limit (OSBL), 243
Oxidation
  catalytic, 302
  destruction of VOCs by, 299
Oxidizer(s)
  catalytic thermal, 301
  recuperative, 5, 295, 296
  regenerative, 5, 297
Oxygen
  deficit ratio, 112, 236
  liquid-phase mass transfer coefficient for, 102
  mass-transfer coefficient of, 125
Ozone
  attainment status, determination of, 10
  non-attainment area requirements, 11, 17

P

Packed-tower scrubbers, 5, 302, 303, 305
PAH, *see* Polyaromatic aromatic hydrocarbons
Paint and pigment industry, discharges from, 339
Parshall flumes, emissions from, 117
Particulate matter (PM), 88, 92
Pathogen destruction, 86
PAVE, *see* Programs to Assess Volatile Emissions
PBMS, *see* Performance based monitoring system
PCBs, *see* Polychlorinated biphenyls
PCDPEs, *see* Polychlorinated diphenyl ethers
PEEP, *see* Pooled Emissions Estimation Program
Perchloroethylene, 38
Performance based monitoring system (PBMS), 4, 222
Permit(s)
  air quality, 346, 357
  federally enforceable state operating, 32, 347
Personnel safety awareness, 28
Pesticide(s), 207, 210
  -grade solvents, 211
  industry, discharges from, 339
Petrochemicals industry, discharges from, 339
Petroleum refineries, 97, 339
PHA, *see* Process hazard analysis
Pharmaceutical industry, 97, 339
Pharmaceutical Research and Manufacturers of America (PhRMA), 24
Photoionization detector (PID), 194
Photoreactive hydrocarbons, 63
PhRMA, *see* Pharmaceutical Research and Manufacturers of America
Phthalate esters, 210
PICs, *see* Products of incomplete combustion
PID, *see* Photoionization detector
Pilot-scale weir models, 124
Plastics industry, discharges from, 339
PM, *see* Particulate matter
Pollutant(s)
  of concern, identification of, 328
  emission of from combustion processes, 88
  secondary, 11
Polyaromatic aromatic hydrocarbons (PAH), 207, 210, 212
Polychlorinated biphenyls (PCBs), 207

Polychlorinated diphenyl ethers (PCDPEs), 211
Polytetrafluoroethylene (PTFE), 209, 219
Pooled Emissions Estimation Program (PEEP), 3, 60, 71, 221
  emission factors, 66, 223, 255
  factors, estimation of VOC emissions by, 229, 230
  study, 175, 235
Pool model, 106
Portland cement, 36
Post-biological treatment units, 62
  chlorination, 62
  effluent filtration, 62
  secondary clarifiers, 62
POTWs, *see* Publicly owned treatment works
PQL, *see* Practical quantitation limit
Practical quantitation limit (PQL), 218
Preliminary/primary treatment
  components of, 61
  unit processes of, 77
Preliminary and primary treatment, VOC emissions from, 117–126
  clarifier surface, 119–123
  emissions at bar racks or screens, 117–118
  emissions at clarifier weirs, 123–125
  grit chambers, 118–119
Prevention of significant deterioration (PSD), 8, 12, 13, 14, 15, 16
Primary sedimentation tanks, 237, 259
Process
  hazard analysis (PHA), 27, 30
  monitoring and control, 344
Products of incomplete combustion (PICs), 88, 91
Programs to Assess Volatile Emissions (PAVE), 246
Proprietary models, VOC emissions estimated using, 239
PSD, *see* Prevention of significant deterioration
PSM, *see* Occupational Safety and Health Administration Process Safety Management
PTFE, *see* Polytetrafluoroethylene
Publicly owned treatment works (POTWs), 1, 36
  air quality compliance
    assessment, 342
    requirements at, 35
  AMSA recommended air toxic compound list for, 70–71
  BACT determination for, 63
  capital improvement plan, 346
  characteristics of air emission from, 320
  comparison of emissions from different, 259
  control technology evaluation methodology, 326
  control of VOC emission from, 254
  cover types for controlling VOC emissions from, 288–289
  development of MACT standards for, 194
  ECHO, 347, 354, 355, 356
  fuel combustion at, 88
  implementation of roadmap at, 357–360
  influents
    concentration of toxicants found in, 43–45
    frequency of occurrence of toxicants found in, 43–45
    model-model parameter combinations predicting VOC emissions rates in, 282
    most frequently occurring VOCs in, 46
    VOC concentration of, 42
  MACT standards, 18, 319
  measurement of nonmethane organic compounds from, 209
  methods for estimating VOC emissions from, 228
  most common biological treatment process used at, 80
  preliminary/primary treatment, 77
  primary HAPs emitted by, 97
  primary sedimentation processes at, 78
  process schematic, 61
  program internal audit, 342
  raw sewage arriving at, 78
  roadmap program element, 358–359
  subgroups, EPA, 18
  unit operations, PEEP factor for, 256–257
  unit processes
    categories of, 60
    screening of emissions from, 261–263
  U.S. EPA surface emission isolation flux chamber at, 198
Pure oxygen activated sludge
  emission factors derived from, 231
  systems, 287
Purge-and-trap GC/MS analysis, 209
Pyridines, 210

Q

QA/QC protocol, *see* Quality assurance/quality control protocol
QSAR, *see* Quality structure activity relationships
Quality assurance/quality control (QA/QC) protocol, 216
Quality structure activity relationships (QSAR), 246

R

RACT, *see* Reasonably available control technology
RAS, *see* Returned activated sludge
RBCs, *see* Rotating biological contactors
RCO, *see* Regenerative catalytic oxidizer
Reasonably available control technology (RACT), 12, 320
Recuperative oxidizers, 5, 295, 296
Refinery
  sludges, emissions factors from belt filter presses treating, 176
  wastewater, 139
    major VOCs found in, 140
    removal efficiencies with, 131
Regenerative catalytic oxidizer (RCO), 297
Regenerative thermal oxidizers (RTOs), 292, 297
  advantages of, 298
  capital costs for, 298
  heat-recovery efficiencies of, 298
Regulatory compliance monitoring, 222
Residual risk analysis, 25
Returned activated sludge (RAS), 146
Risk assessment, use of direct assessment technique for, 221
RMP, *see* United States Environmental Protection Agency Clean Air Act Risk Management Plan
Rotating biological contactors (RBCs), 62, 80, 81, 155, 156
  factors affecting emissions from, 82
  fate of VOCs in, 168
  sources of emission, 83
  studies, 162
  test apparatus, 165
  ventilation, 82
RTOs, *see* Regenerative thermal oxidizers

S

Sample
  chain-of-custody, 216
  integrity, 216
  interfering compounds extracted from, 211
  transport, 217
Sampling methodology, 191–205
  compositing of air samples, 204–205
  compositing methodology for liquid VOC samples, 202–204
  liquid sampling, 192
  sampling for ambient air and non-combustion point sources, 192–200
  sampling of combustion sources, 200–202
  solids sampling, 192
SCADA system, *see* Supervisory control and data acquisition system
SCAQMD, *see* South Coast Air Quality Management District
Schmidt number, 105, 120, 122
Scrubber(s)
  carbon
    advantages of, 306
    disadvantages of, 306
  cross-flow, 302
  mist, 303
    disadvantages of, 304
    schematic, 304
  packed-tower, 5, 302, 303, 305
  wet, 301
SEAM model, *see* Secondary emission assessment model
Secondary clarifiers, 231, 237, 259, 262, 279
Secondary emission assessment (SEAM) model, 243
Secondary lead smelting, 36
Secondary pollutant, 11
Sedimentation, primary, 261
Selection ion mode (SIM), 206
Semiconductor industry, discharges from, 339
Semivolatile organic sampling train (SMVOST), 201, 202
Sewage sludge
  compost (SSC), 310
  incineration, 34
Sewer(s)
  classification of receiving wastewater, 42
  commercial, VOC concentration of, 42
  depressed, 75
  emissions, description of, 101
  experiments involving controlled injection of krypton, 104
  headspace, ventilation in, 99
  interceptor, 75
  lateral, 75
  networks, distribution of emissions from, 114
  overflow areas, 41
  reaches
    continuous ventilation forced along, 77
    mass transfer occurring along, 99
  system(s)
    air flow rate exhausting from opening in, 100
    construction of, 60
    experiments completed on laboratory-scale, 110
  tracer studies, 103
  trunk, 75
  ventilation, 76, 110, 111

  VOC concentrations in, 42
Sewers, VOC emissions from, 97–116
  air exchange rates, 107–111
  drop structures, 106–107
  emission mechanisms, 99
  factors affecting sewer VOC emissions, 98–99
  field monitoring, 105
  modeling, 111–113
    CORAL+, 112
    naUTilus, 113
    screening techniques, 111–112
    TOXCHEM+, 113
    WATER9, 113
  theoretical considerations, 99–103
  tracer studies, 103–105
Sharples centrifuge, 180
Shell-and-tube heat exchanger, 292
Shock loading, 101
Silica gel traps, 202
SIM, *see* Selection ion mode
SIPs, *see* State Implementation Plans
Sludge(s)
  activated, 148
  anaerobic digestion of, 86
  cake-storage, 259
  conveyor, 238, 259
  dewatering
    centrifuges, 238, 259
    parameter estimate for VOC fraction emitted in, 186
  diffused air activated, 61, 257, 262
  drying beds, emission factors derived from, 233, 236
  high purity oxygen activated, 62
  mass reduction, 86
  refinery, emissions factors from belt filter presses treating, 176
  returned activated, 146
  streams, toluene in, 178
  truck loading, 259
  waste activated, 146
SMVOST, *see* Semivolatile organic sampling train
SOCMI, *see* Synthetic Organic Chemical Manufacturing Industry
Solid bowl centrifuge, schematic of, 173
Solids handling, 85–88
  emission mechanisms, 87
  factors affecting emissions for, 88
  process description, 86–87
  unit processes, 62
    additional stabilization, 62
    aerobic digestion, 62
    anaerobic digestion, 62
    dewatering, 62
    dissolved air flotation thickening, 62
    drying, 62
    lagooning, 62
    storage, 62
Solvents, pesticide-grade, 211
SOPs, *see* Standard operating protocols
Sorbent tubes, 200
Sorption, 149, 151, 246
Source characterization and VOCs of importance, 59–72
  collection systems, 60
  other characterization data, 67–71
    AMSA list, 67–71
    1990 Clean Air Act Amendments Title III list, 67
    Synthetic Organic Chemical Manufacturing Industry, Hazardous Organic NESHAP list, 67
  POTWs, 60–62
    biological treatment, 61–62
    combustion sources, 62
    post-biological treatment, 62
    preliminary/primary treatment, 61
    solids handling, 62
  selection of important VOCs, 62–67
    nonvolatile and degradable compounds, 66
    nonvolatile and nondegradable compounds, 67
    recommended classification strategy, 63–66
    total hydrocarbons, 67
    volatile and degradable compounds, 66
    volatile and nondegradable compounds, 66
South Coast Air Quality Management District (SCAQMD), 4, 15
  guidelines, 220
  regulations, 223
  Rules, 191
  U.S. EPA methods modified by, 201
SSC, *see* Sewage sludge compost
Stack gas velocity, detection of, 194
Standard operating protocols (SOPs), 216
Standards, area source categories subjected to, 36
State Implementation Plans (SIPs), 8
Stickney aerated grit chambers, 277
Stickney WRP VOC emissions, 270–271
  computed by BASTE, 272–273
  computed by TOXCHEM, 274
Storage sludge cake, 238
Street inlets, 75
Subsurface diffusion aeration, 148, 245
Summa canister sampling system schematic, 196
Sunlight, photochemical reactions involving, 11

Supervisory control and data acquisition (SCADA) system, 245
Surface volatilization model, 139
Synthetic organic chemical manufacturing, discharges from, 339
Synthetic Organic Chemical Manufacturing Industry (SOCMI), 67
Synthetic rubber industry, 36, 339

T

TACs, *see* Toxic air contaminants
Tapwater
  experiments, 132
    concentrations measured in, 134
    percent volatilized vs. Henry's Law coefficient, 136
  mass balance analysis, volatilization results from dosed, 135
TCLP, *see* Toxicity characteristic leaching procedure
Tenax trap, 202
Tentatively identified compounds (TICs), 264
Tetrachloroethene, emission rates of, 66
Textile industry, discharges from, 339
TFs, *see* Trickling filters
Thermal treatment, costs of, 293
THMs, *see* Trihalomethanes
TICs, *see* Tentatively identified compounds
Top-down BACT procedure, U.S. EPA, 320, 321, 324, 326, 329
Top-down RACT example and worksheets, 363–379
Total hydrocarbons, 67
TOXCHEM, *see* Toxic Chemical Modeling Program for Water Pollution Control
Toxic air contaminants (TACs), 220
  detection of, 220, 221
  emissions, guidelines for quantifying, 220
Toxic Chemical Modeling Program for Water Pollution Control (TOXCHEM), 3, 91, 94, 123, 147, 240, 264, 274
Toxicity characteristic leaching procedure (TCLP), 223
Tracers, volatile, 104
Treatment plants, NYCDEP, range of VOC concentrations in, 50
Trichloroethylene, 38
Trickle-bed bioreactors, 307
Trickling filters (TFs), 62, 80, 155, 237, 259
  emission factors derived from, 231
  factors affecting emissions from, 82
  fate of VOCs in, 167
  process schematic, 156
  sources of emission, 83
  stripping by, 290
Trihalomethanes (THMs), 84
TriTAC
  emission factors, 229, 239, 260, 261–263
  Guidance Document, 71
Trunk sewers, 75

U

United States Environmental Protection Agency (U.S. EPA), 3, 8
  ambiguity of HAP emissions addressed by, 221
  AP-42 emission factors, 240
  Clean Air Act Risk Management Plan (RMP), 25
  Fate and Treatability Estimator model, 247
  40-City Study, 45
  FTIR Method recommended by, 214
  Industrial Combustion Coordinated Rulemaking (ICCR) program, 214
  Method 18, 208
  methods, modified, 201
  Method TO-14, 206
  Office of Air Quality Planning and Standards (OAQPS), 330
  POTW subgroups, 18
  PSD guidelines, 12
  public domain model, 3
  recuperative incinerator cost estimate by, 297
  surface emission isolation flux chamber, 196, 198
  top-down BACT procedure, 320, 321, 324, 326, 329
Unit processes and emission, 73–95
  biological treatment, 79–82
    emission mechanisms, 81
    key factors affecting emissions, 81–82
    process description, 80–81
  collection systems, 74–77
    emission mechanisms of collection systems, 75–76
    key factors affecting emissions of collection systems, 76–77
    process description of collection systems, 74–75
  combustion processes, 88–91
    emission mechanisms, 90–91
    key factors affecting emissions, 91
    process description, 88–90
    products of incomplete combustion, 91
  estimating emissions from POTWs, 91–94

- post-biological treatment, 82–85
  - emission mechanisms, 83–84
  - key factors affecting emissions, 84–85
  - process description, 82–83
- preliminary/primary treatment, 77–79
  - emission mechanisms, 78–79,
  - key factors affecting emissions, 79
  - process description, 77–78
- solids handling, 85–88
  - emission mechanisms, 87
  - key factors affecting emissions, 88
  - process description, 86–87

Urban Air Toxics Strategy, 319
U.S. air quality regulations, 7–36
- Integrated Urban Strategy, 33–34
- other regulations, 34–36
- POTW MACT standards, 18–30
  - accidental release and prevention program, 25–30
  - residual risk analysis, 25
- Title I, 10–17
  - new source performance standards, 15–17
  - new source review and permitting in non-attainment areas, 15
  - prevention of significant deterioration, 12–13
  - PSD applicability, 13–15
  - reasonably available control technology, 12
- Title III, 17
- Title V, 30–33

U.S. EPA, *see* United States Environmental Protection Agency
U.S. Water Environment Research Foundation, 304, 309

V

Vapor phase controls
- nontraditional, 287, 315
- thermal treatment, 291
- traditional, 286, 315

Velocity controlled grit chambers, 118
Ventilation, mechanisms affecting, 107
Venturi scrubbers, 298
VOA, *see* Volatile organic analysis
VOC emissions, *see also* Emissions
- control, roadmap approach to, 341–344
  - benefits of proactive approach, 343–344
  - purpose of roadmap, 341
  - roadmap approach, 342–343
  - roadmap concept, 341–342
- information gaps, 339
- major factors affecting, 339–340
  - relationship to odor control, 340
  - site-specific considerations, 339–340
- rate(s)
  - computing of using noncomprehensive models, 268
  - direct measurement of, 278
  - model-computed annual, 283
  - outputs, comparison of, 266
  - predicted, 111
- Stickney WRP, 268, 270–271
- total, 267

VOCs, *see* Volatile organic compounds
VOHAPs, *see* Volatile organic HAPs
Volatile organic analysis (VOA), 202, 205
Volatile organic compounds (VOCs), 1
- analysis, gas phase samples for, 132
- background gas phase concentrations of, 163
- biodegradation
  - losses of in aeration tank, 151
  - rate, 82
- concentrations
  - non-listed, 40
  - waste stream, 130
- consumer products containing, 97
- deficit ratio, 241
- destruction of by oxidation, 299
- direct measurement of emitted, 247
- emission of from DAF units, 127, 131
- fate models, 145
- gas phase
  - emissions, 141
  - resistance, 108
- Henry's law constant of, 103
- industrial discharges containing, 38
- -laden air streams, poor choices for treating, 293
- liquid transfer coefficient for, 123
- losses, prediction errors, 108
- mass discharges of to municipal wastewater collection systems, 98
- poorly degraded, 166
- removal, 109, 157, 164, 314
- samples, compositing methodology for liquid, 202
- stripping, 109
- substrate
  - concentration, 157
  - mass transfer parameter for, 162
- tracer method, estimation of VOC emissions by, 229, 248
- train, schematic of sampling method for, 203
- transfer studies, 174
- volatilization
  - factors influencing, 76

    occurrence of, 76
Volatile organic HAPs (VOHAPs), 194
Volatile organic sampling train (VOST), 201, 202
Volatilization
  in activated sludge systems, 148
  BASTE model simulation of, 152
  biosolids surface, 87
  coefficients, 169
  model
    predictions of, 160
    surface, 139
  VOC losses due to, 276
Vortex-type grit chambers, 118, 119
VOST, *see* Volatile organic sampling train

W

WAS, *see* Waste activated sludge
Waste activated sludge (WAS), 146
Wastewater(s)
  concentrations of candidate compounds in, 138
  disposal of, 1
  dosed, 135
  experiments
    percent volatilized in dosed, 138
    volatilization examined by, 132
  flow rate of, 109, 110
  fluid properties, 98
  industrial solvents found in, 39
  oil and grease removal from, 141
  oil refinery, 139
  organics in, 79
  process conditions for experiments conducted with, 134
  reconstituted refinery, 140
  refinery
    major VOCs found in, 140
    removal efficiencies with, 131
  rise and fall, ventilation and, 107
  sources of VOCs in, 38
  statistical comparison of detected VOCs in, 51–55
  treatment processes
    disinfection in, 83
    pilot scale testing of, 163
    residual solids from, 171
  velocity, 101
  VOC emissions from, 98
Wastewater, occurrence of volatile organic compounds in, 37–57
  concentrations of VOCS in wastewater, 42–50
    Association of Metropolitan Sewerage Agencies, 47
    East Bay Municipal Utility District, 47
    EPA 40-city study, 45–46
    New York City study, 49–50
    Ontario, Canada study, 47
    RTI study, 46
    VOC concentration in domestic vs. industrial sewerage systems, 42
    VOC concentration of POTW influents, 42–45
  sources of VOCs in wastewater, 38–41
    chemical and biogenic reactions occurring during treatment, 41
    commercial establishments, 39
    household and consumer products, 39
    industries, 38–39
    surface runoff, 39–41
    water supply, 38
Wastewater treatment facilities, VOC emissions from, 253–284
  comparative evaluation of performance of comprehensive fate models, 267–282
    Metropolitan Water Reclamation District of Greater Chicago studies, 269278
    New York City Department of Environmental Protection studies, 278–282
  comparative evaluation of performance of noncomprehensive fate models, 267
  quantitation of VOCs by emission factors, 254–260
    JEIO emission factors, 255–260
    PEEP emission factors, 255
    TriTAC emission factors, 260
  VOC emissions from POTWs by general fate models, 260–267
WATER7 model, 269, 276
WATER8 model, 91, 94, 121, 145, 148, 240, 279
WATER9 model, 91, 94, 113, 125, 240, 242
Water pollution control plants (WPCPs), 49, 264, 278
Water reclamation plant (WRP), 229, 282
Weir(s)
  clarifier, 123
  configuration, 79
  drops, 290
  emission factors determined for, 235
  models, pilot-scale, 124
  oxygen deficit ratios of, 235
Wet scrubbing, 5, 300, 301
Wind
  eduction, 76, 77, 107
  effect of on mass-transfer coefficient of gases, 123
  tunnel, 198, 199

Windows-based model, 244
WPCPs, *see* Water pollution control plants
WRP, *see* Water reclamation plant

Y

Yard waste compost (YWC), 310
YWC, *see* Yard waste compost

Water Science, Engineering, and Technology

VOC Emissions from Wastewater Treatment Plants

Although primarily concerned with the treatment of wastewater and water quality, publicly owned treatment works (POTWs) are required to be in compliance with the Federal Clean Air Act and an increasingly stringent series of Clean Air Act Amendments to control emissions of odors, criteria pollutants, and volatile organic compounds (VOCs). How POTWs demonstrate, document, or show compliance with federal and state or local quality laws and regulations can vary significantly. **VOC Emissions from Wastewater Treatment Plants: Characterization, Control, and Compliance** provides the tools, concepts, policies, and information you need to develop an air quality compliance plan and maintain the plan's viability.

With contributions from a panel of experts and authoritative editorial guidance, the book reflects many approaches based on various air quality compliance and assessment conditions and experiences. The editors use this body of knowledge to develop a clear picture of how to design, set up, and maintain a successful air quality compliance program. Building on this foundation, **VOC Emissions from Wastewater Treatment Plants: Characterization, Control, and Compliance** shows you how to create a comprehensive, complete program that includes POTW-specific air emissions inventory information, measurement techniques, and viable control options.

Features

- Contains comprehensive information on the subject of VOC emissions from POTWs
- Describes models of emission factors that demonstrate what to expect when models are used for the estimation of VOCs from specific wastewaters
- Presents information on VOC emissions from various unit processes such as sewers, preliminary and secondary clarifiers, activated sludge and attached growth systems, sludge treatment, and combustion devices
- Provides a roadmap approach to air pollution abatement compliance that you can use to determine human resources needs

TX68209
ISBN 1-56676-820-9
90000
9 781566 768207

Lewis Publishers
www.crcpress.com